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NOVEL SUBSTITUTED TETRATHIA[7]HELICENES BY DIRECT FUNCTIONALIZATION OF THE HELICAL SYSTEM OR PHOTOCYCLIZATION OF SUBSTITUTED 1,2-(BIS-BENZODITHIENYL)ETHENES

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Dedicated, with admiration, to Professor Ryoji Noyori on the occasion of his 70th birthday.

Abstract – In this work we report the synthesis of several new tetrathia[7]helicenes ([7]THs) functionalized with different electron-donor (ED) and electron-acceptor (EA) substituents in the positions 2,13 (the α positions of terminal thiophene rings) and/or 7,8 (on the central arene ring of the helical system). Some substituents were chosen on the basis of theoretical calculations performed on [7]THs to predict the best groups for applications in optoelectronics; some others were conceived to endow helicenes with appropriate groups in view of their insertion into polymeric structures.

INTRODUCTION

Helicenes[1] are polyconjugated π-systems in which a minimum of five orthofused polycyclic aromatic or heteroaromatic rings are angularly arranged to generate a chiral, stable, non planar helical system, thus allowing the existence and the separation of *P* and *M* enantiomers.

In 1955, Newman[2] discovered the chirality of helicenes, and the properties of these compounds have been even recently reviewed.[1c]

Carbohelicenes only include benzene rings in their structure, while in heterohelicenes[1b,c,i] one or more aromatic rings are heterocycles as in molecule **1**, the tetrathia[7]helicene (Figure 1), in which thiophene rings alternate benzene rings.

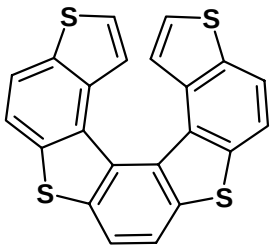

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Figure 1. Tetrathia[7]helicene

The tetrathia[7]helicene ([7]TH) **1**[3] is the parent compound of a class of heterohelicenes potentially very interesting for applications in optoelectronics as well as new chiral ligands for both organic and organometallic catalysis.[4] In fact, analogously to carbohelicenes, they exhibit intrinsic asymmetry, the helix is configurationally stable and therefore *M* and *P* enantiomers can be obtained. In addition, they combine the presence of the above-mentioned chiral $\tilde{\pi}$-conjugated system with the existence of two terminal thiophene rings which allows regioselective functionalization of the helical system. As a consequence, the insertion of appropriate substituents can modify and tune both electronic and optical properties, or endow the chiral helix of appropriate functional groups for use in catalysis. Progress in the above research area requires appropriate, efficient and flexible synthetic methodologies to introduce substituents in a regioselective manner.

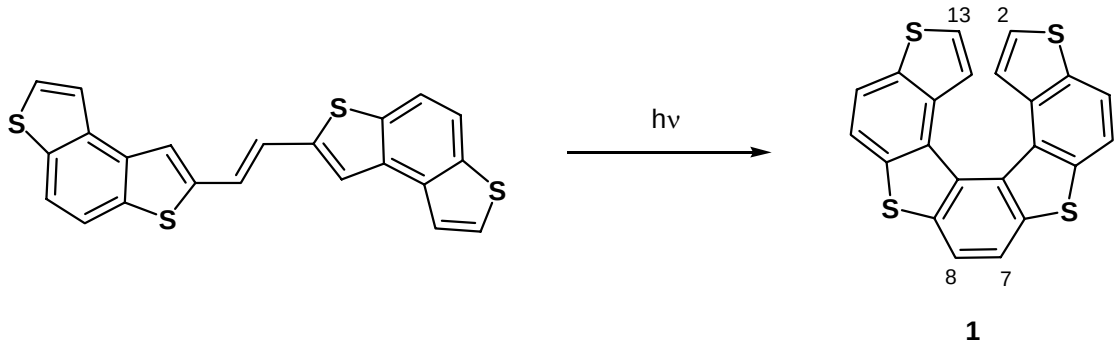
Although [7]TH is known for a long time,[3] still today many efforts are directed to the set up of synthetic methodologies with the aim of improving the preparation of tetrathiahelicene derivatives.[1b,c,5]

During the last few years we have been given a contribution to the mentioned synthetic work,[5] which was addressed towards the preparation of differently substituted helicenes and the study of their properties[6] in view of possible applications in fields such as materials with electro optical characteristics or catalysis mentioned above.

The most popular and efficient route to the helical core of [7]TH is the construction of the central benzene ring through the photochemical cyclization of the 1,2-(bis-benzodithienyl)ethene (Scheme 1). Therefore, to obtain functionalized helicenes, two general synthetic pathways can, in principle, be envisaged: i) preparation of the appropriately substituted 1,2-(bis-benzodithienyl)ethenes to be photocyclized to the corresponding substituted [7]TH,[1c] and *ii)* functionalization of the [7]TH itself.[5a,b,e]

The first route requires the substituents present on the 1,2-(bis-benzodithienyl)ethene being stable to photochemical cyclization, while the second one is more versatile even if it allows the introduction of functional groups mainly in positions **2** and **13**.

In this paper we describe the synthetic work we did in view of obtaining a variety of tetrathia[7]helicenes substituted with electron-donor (ED) and electron-acceptor (EA) groups in the positions 2,13 and/or 7,8.



Scheme 1. Photochemical cyclization of 1,2-(bis-benzodithienyl)ethene to helicene **1**

In fact, theoretical calculations[7] predicted that the presence of ED and EA substituents in the above-mentioned positions should have a strong effect on optoelectronic properties of tetrathiahelicenes. In particular, the compounds studied and reported in this paper are shown in Chart 1.

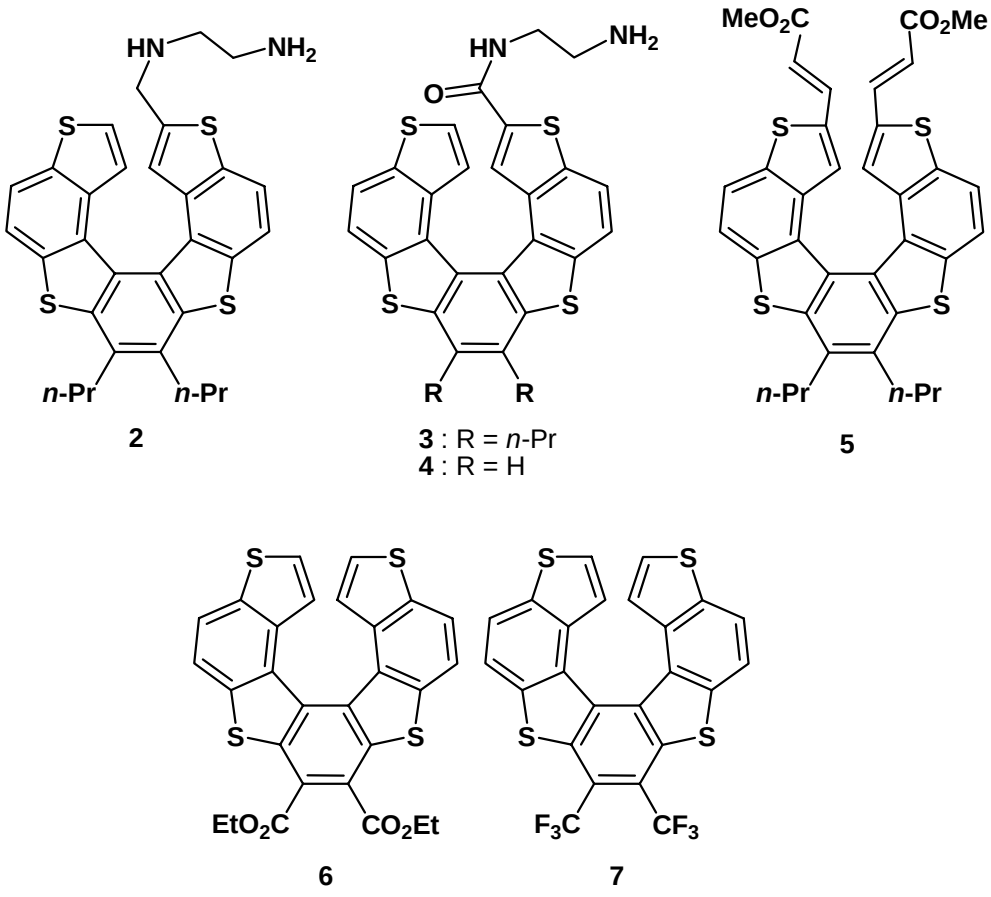


Chart 1. Tetrathia[7]helicenes **2-7** prepared

Compound **2** has an electron-donor substituent at the position 2, while compounds **3** and **4** bear, at the same position, one electron-acceptor group. In compound **5** two ethoxycarbonyl moieties are conjugated to the π-helical system through a carbon-carbon double bond. Finally, compounds **6** and **7** have two

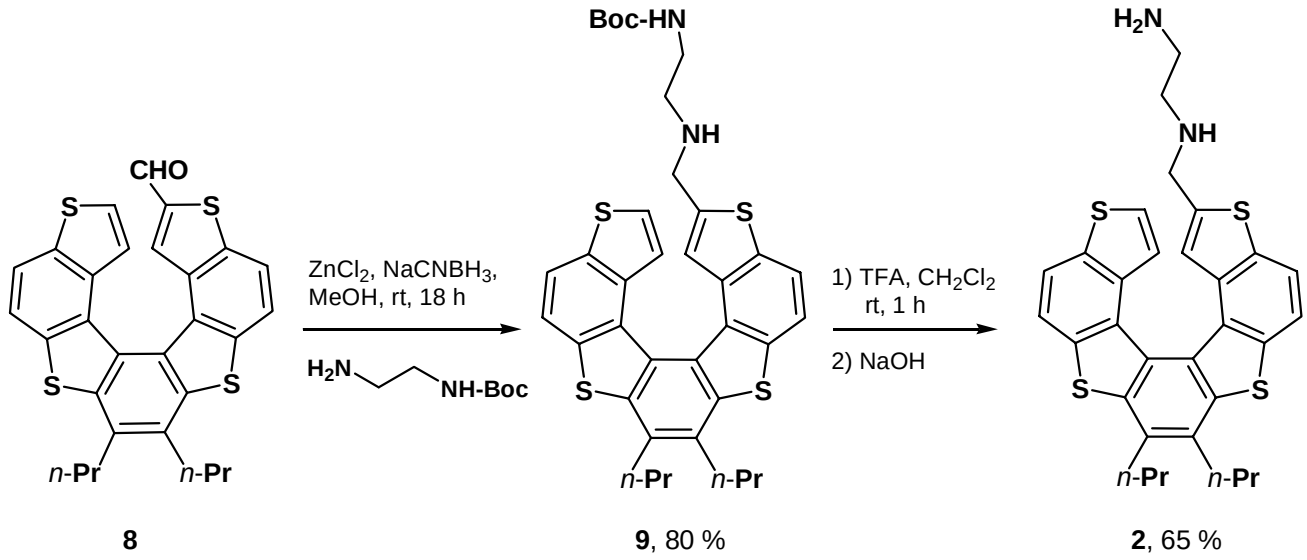
electron-acceptor groups in the central phenyl ring. The *n*-propyl chains in compounds **2**, **3** and **5** assure a better solubility in organic solvents. The presence of primary amino groups in compounds **2-4** and of the αβ-unsaturated acrylic chain will allow the use of these helicene derivatives as co-monomers in the synthesis of polymers obtainable using the Michael addition strategy.[8]

Two different synthetic strategies have been studied for the synthesis of helicenes **2-7**: compounds **2-5** have been prepared by direct functionalization of positions 2 and 13 of the helical system, while compounds **6** and **7** arise from 1,2-(bis-benzodithienyl)ethenes (precursors of helicenes) already containing the functional groups.

RESULTS AND DISCUSSION

Functionalization of helicenes

The direct and regioselective functionalization of the 2,13 positions of [7]TH is easily accomplished by deprotonation with a strong base and reaction of the formed mono- or dianion with electrophilic reagents, as already reported.[5a,b,e] Following this protocol, helicene **2** was prepared as shown in Scheme 2. The monoaldehyde **8**, previously reported by us[5b], was reacted with *N*-Boc-ethylenediamine in a reductive amination reaction with $ZnCl_2$ and $NaCNBH_3$ in methanol at room temperature. The helicene **9** was isolated in 80% yield, as white solid, and then deprotected with trifluoroacetic acid in CH_2Cl_2 to give the target helicene **2** in 65% yield, as a white solid.

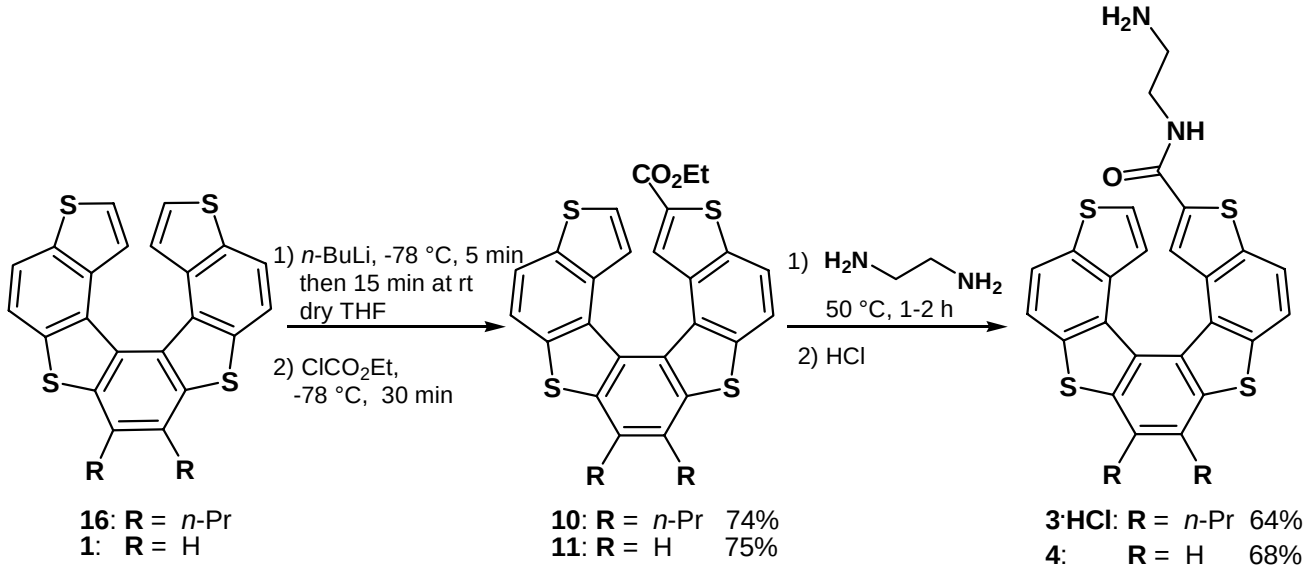


8 **9**, 80 % **2**, 65 %

Scheme 2. Synthesis of the aminoethylaminomethylhelicene **2**

The synthesis of the aminoethylamidohelicenes **3** and **4** (Scheme 3) was performed by reacting the monoesters **10**[5b] and **11** with ethylenediamine at 50 °C for two hours. Product **4** was isolated as free amine in 68 % yield, while compound **3** was recovered as hydrochloride salt in 64% yield. The monoester **11**, not

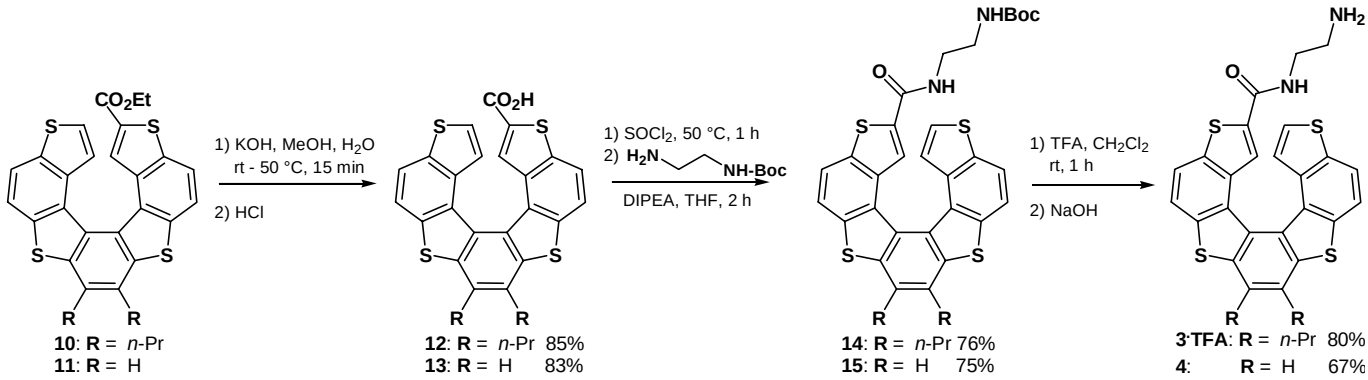
previously reported in the literature, was prepared as reported in Scheme 3, that is, by deprotonation of helicene **1** with one equivalent of base, and reaction of the monoanion thus formed with ethyl chloroformate.



Scheme 3. Synthesis of tetrathia[7]helicenes **3** and **4**

Due to the long and tedious purification of **3** and **4** from the ethylenediamine (used as the reaction solvent), the alternative route reported in Scheme 4 was also developed. In this strategy the final amide bond was formed through the classical reaction of the appropriated acyl chloride with ethylenediamine.

In particular, the monoesters **10** and **11** were hydrolyzed in basic medium to give, in high yields, the corresponding carboxylic acids **12** and **13** which were then transformed into the corresponding acyl chloride derivatives and in situ reacted with the *N*-Boc-ethylenediamine in the presence of DIPEA, in THF solution at 50 °C. In this way amide derivatives **14** and **15** were obtained in 76% and 75% yield respectively. Treatment with trifluoroacetic acid of the helicenes **14** and **15** in CH_2Cl_2 solution at room temperature for one hour, afforded the final helicene **3** as trifluoroacetic acid salt in 80% yield and, after basic work-up, the amino ethyl amido helicene **4** in 67% yield.

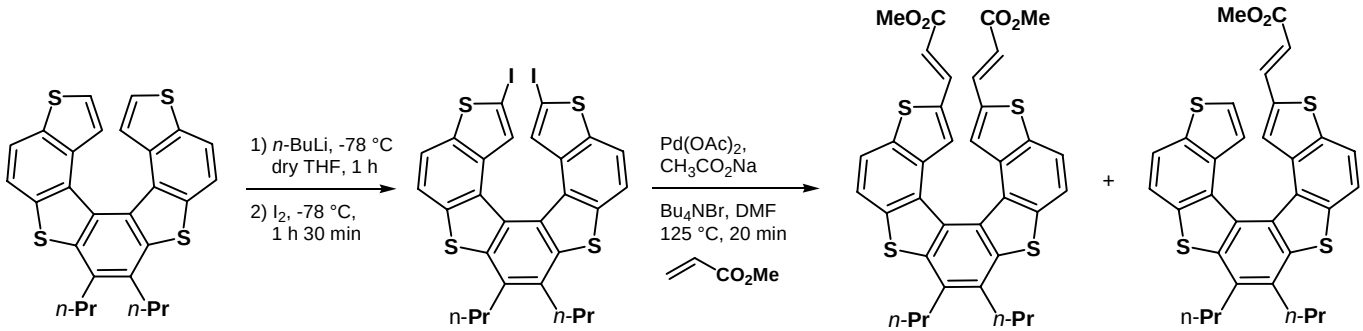


Scheme 4. Synthesis of the aminoethylamidohelicenes **3** and **4**

Even if, following Scheme 4, the overall yield in helicenes **3** and **4** was a little bit lower than that obtained using the method reported in Scheme 3, this last methodology resulted easier in term of isolation and purification of the final helicenes.

The helicene **5**, in which the two ester functions are connected to the helix through an ethylene bridge, was synthesised as reported in Scheme 5. The dianion of helicene **16**, obtained by deprotonation with *n*-BuLi, was reacted with iodine to give the corresponding diiodo-[7]TH **17** in quantitative yield.

The presence of the two halogen atoms allowed the Heck coupling of **17** with vinyl acetate; the reaction was performed in DMF solution and in the presence of $Pd(OAc)_2$ as the catalyst, sodium acetate and tetrabutylammonium bromide. (Scheme 5)[9]

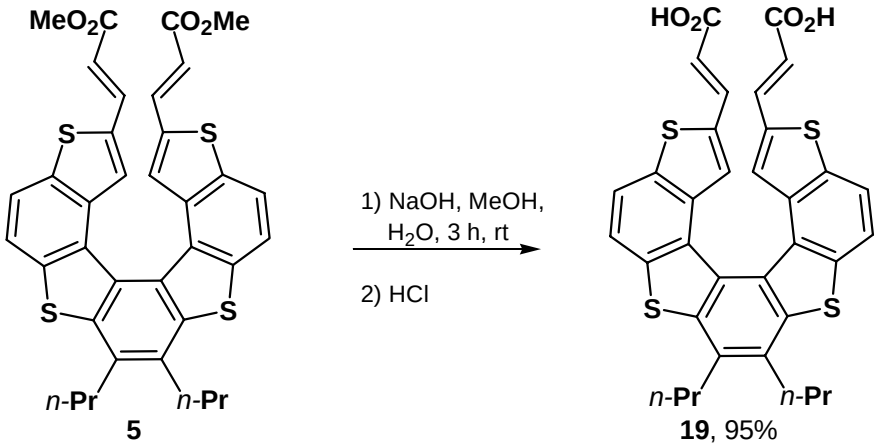


Scheme 5. Synthesis of helicene **5** by Heck coupling

Besides diester **5,** which was obtained in 94% yield, a 4% of the monoester **18** was also isolated.

We used helicene **5** elsewhere, as co-monomer to include helicenes in a polymeric chain.[8]

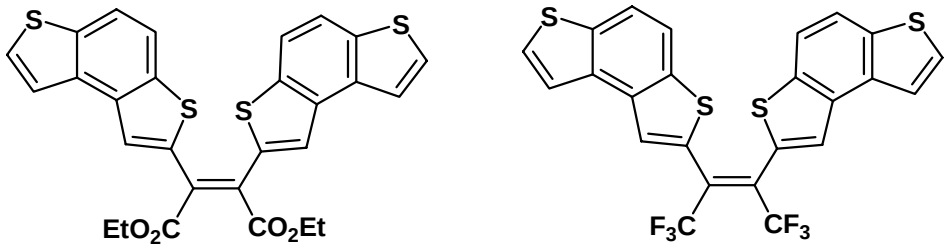
Basic hydrolysis of **5** gave the dicarboxylic acid derivative **19** in 95% yield. (Scheme 6) The interest for helicenes bearing hydroxycarbonyl groups resides in the possibility of generating diastereoisomeric salts for their separation into enantiomers.



Scheme 6. Hydrolysis of 7,8-di-*n*-Pr-2,13 di-vinylcarboxymethyltetrathia[7]helicene **5**

Synthesis of 1,2-(bis-benzodithienyl)ethenes

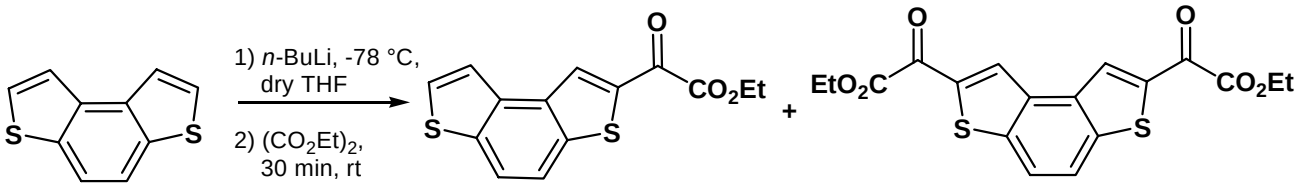
The synthetic strategy utilized for obtaining tetrathiahelicenes **6** and **7,** bearing two substituents in the positions 7 and 8 of the central phenyl ring (Chart 1), was different from that described above for helicenes **2-5**. In fact, due to the presence of three equivalent phenyl rings in the [7]TH system, it is not possible to functionalize positions 7 and 8 of the helical system in a regioselective manner. Owing to the fact that tetrathiahelicenes are obtained through the photochemical cyclization of 1,2-(bis-benzodithienyl)ethenes (Scheme 1), we synthesized alkenes **20** and **21**, bearing two substituents on the double bond as suitable precursors of helicenes **6** and **7** (Chart 2).



20 **21**

Chart 2

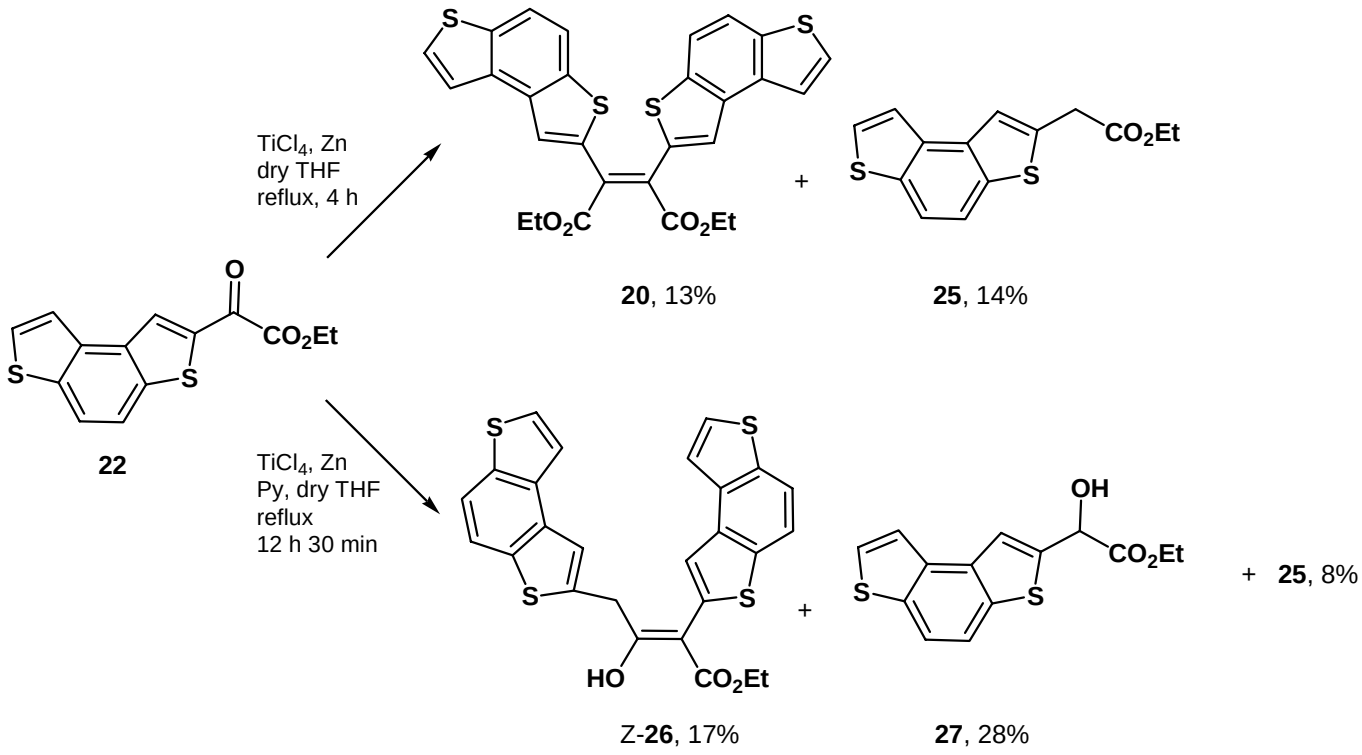
Thanks to the symmetry of alkenes **20** and **21**, a suitable methodology for their synthesis could be a reductive coupling of carbonyl precursors. The synthesis of alkene **21** was already reported by us[5b] through the McMurry coupling of the benzodithienyl trifluoromethyl ketone. Following the same strategy, for the synthesis of **20** we studied the McMurry coupling on the ethyl benzodithienyl glyoxylate **22** (Scheme 7). Compound **22,** not previously reported in literature, was synthesised starting from the benzodithiophene **23,** which, after deprotonation of the α position of the terminal thiophene ring to give the corresponding monoanion, was reacted with diethyloxalate[10] in THF solution. Compound **22** was obtained as a yellow-orange solid in 65% yield after purification with flash column chromatography on silica gel. In addition, we also isolated the disubstituted derivative **24** in 10% yield, as orange solid. (Scheme 7) Compound **22** was then submitted to McMurry coupling reaction, by *in situ* generating the low valence Ti



23 **22**, 65% **24**, 10%

Scheme 7. Synthesis of benzodithienyl glyoxylate **22**

species from $TiCl_4$ with Zn, and refluxing the reaction mixture for 4 hours in THF solution (Scheme 8). Standard work up afforded alkene **20**, in 13% yield as an orange solid, besides the benzodithienylethyl acetate **25**, formed by reduction of ketone **22**, in 14% yield. The ^{1}H NMR analysis of alkene **20** shows the presence of only one isomer.



Scheme 8. McMurry coupling on ketone **22**

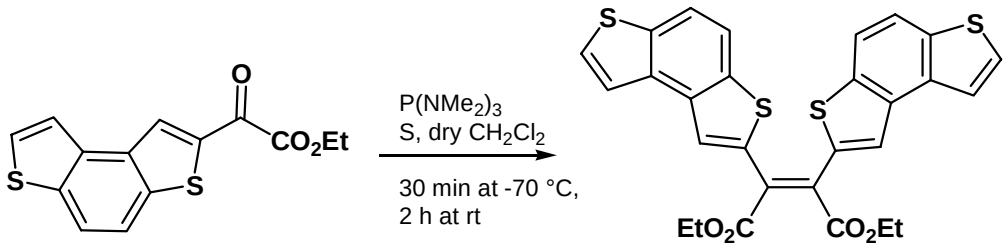
In an attempt of improving the yield of alkene **20**, the reaction was repeated in the presence of pyridine (1.5 eq), but, in this case compound **20** was not formed at all. Instead, from the column chromatography on silica gel of the crude reaction mixture we only isolated products **26**, **27** and **25** in 17%, 28% and 8% yield respectively (Scheme 8). The hydroxyester **27** arises from a partial reduction of ketoester **22**, while the formation of alkene **26** can be explained by assuming a McMurry coupling between the ester **25 (**the Clemmensen-type reduction product) and the starting ketoester **22,** followed by dealkylation of the ethoxy group. The preferred enol form adopted by **26** can be justified considering the high degree of conjugation of such hydroxy system. Compound **26** was isolated as single isomer, and was completely characterized by analytical and spectroscopic data.

The results reported in Scheme 8 could be rationalized considering that ketone **22**, bearing the electron-withdrawing ester group, is much more prone to a reduction reaction to give compounds **25** and **27** than to give the expected reductive coupling. It is worth while to note that in the literature just one example of McMurry coupling on electron-poor carbonyl moieties is reported.[11]

The unsatisfactory results obtained using the McMurry coupling, prompted us to explore an alternative

route for the synthesis of alkene **20**. A different methodology reported in the literature[12] for the coupling of α-ketoesters derivatives utilizes the combination of tris(dimethylamino)phosphine and sulphur in methylene chloride solution.

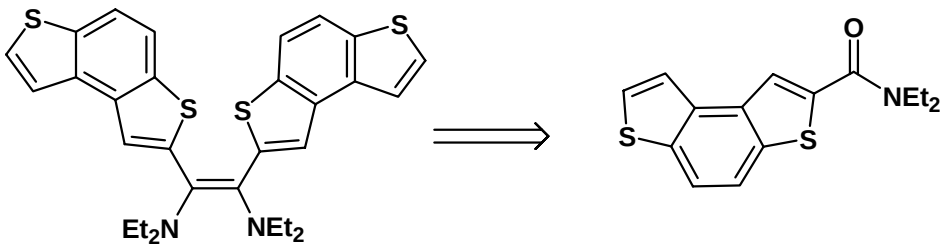
Therefore, the ketoester **22** was reacted in the above mentioned system (Scheme 9) affording, after 2 hours at room temperature, the expected alkene **20** in 80% yield, as a mixture of diastereoisomers in 75:25 ratio, besides a 18% of the starting compound **22**.



22 **20**, 80%
d.r. 75:25

Scheme 9. Synthesis of 1,2-bis(ethoxycarbonyl)-1,2-bis(benzodithien-2'-yl)ethene **20**

The methods reported above yielded 1,2-(bis-benzodithienyl)ethene substituted on the double bond with electron-withdrawing groups. In principle, the same reductive coupling methodologies could be employed to insert electron-donating groups on the same positions. In particular, we considered the diethylamino group and we therefore studied an appropriate synthetic route for the preparation of compound **28**. It is known that the deoxygenative coupling of amides with the Sm/SmI_2 system, provides a way for preparing *vic*-diaminoalkenes.[13] In view of utilizing this method, the appropriate precursor of alkene **28** was the amide **29** (Scheme 10).

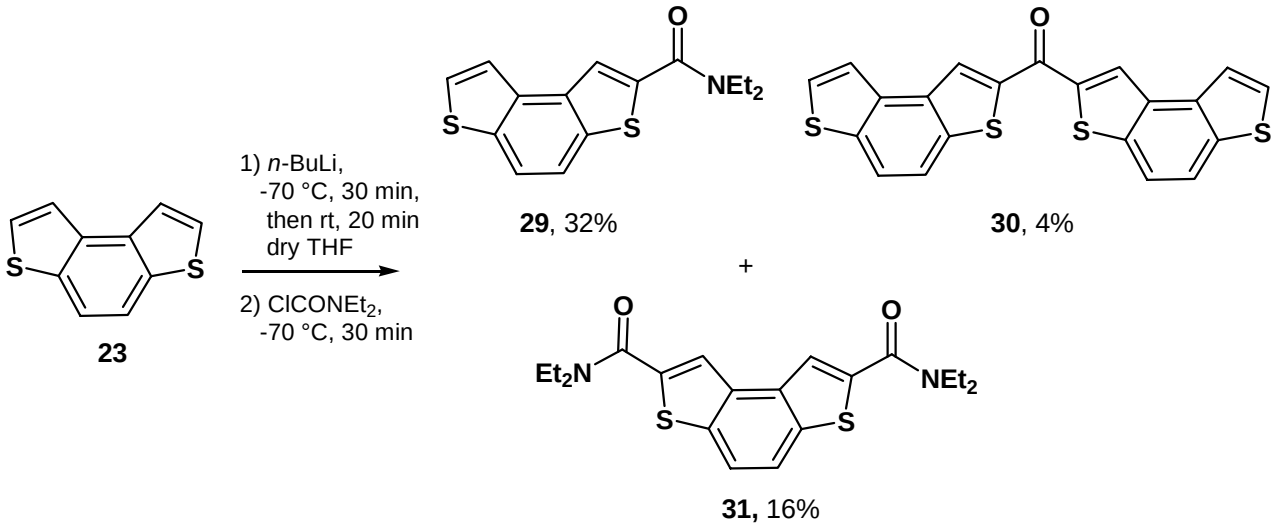


28 **29**

Scheme 10

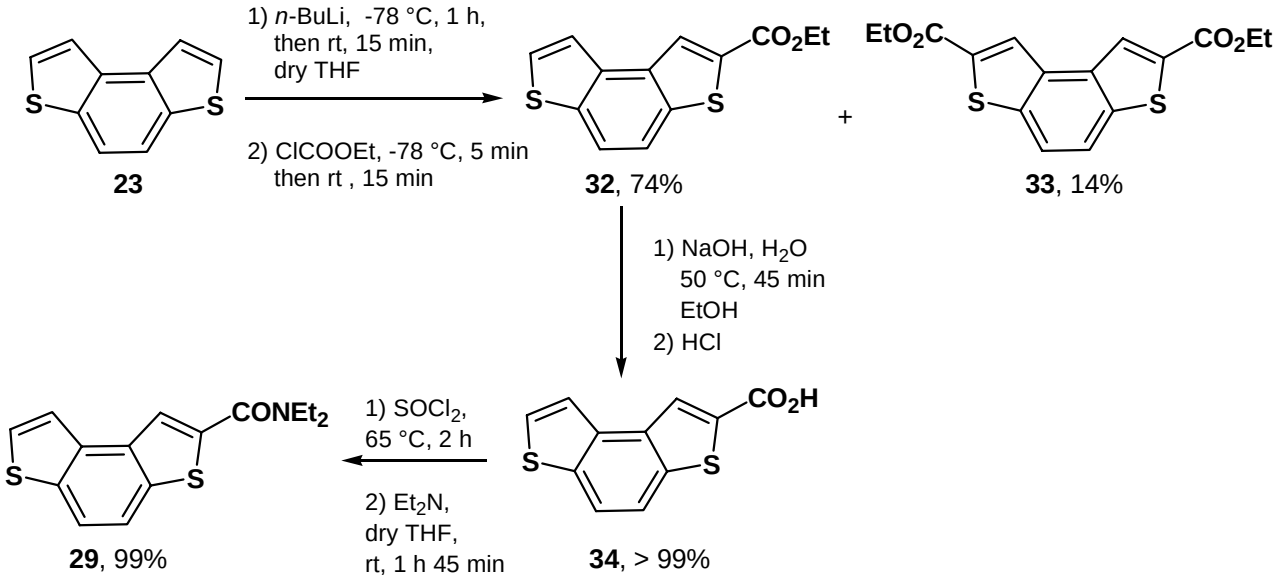
The most simply and direct way to obtain **29**, would be the introduction of the diethylaminocarbonyl moiety by reacting the monoanion of benzodithiophene **23** with diethylcarbamoyl chloride.[14] However, when we utilized this route (Scheme 11) we obtained the expected amide **29** in only 32% yield, besides

the two by-products **30** and **31** in 4% and 16% yields respectively.



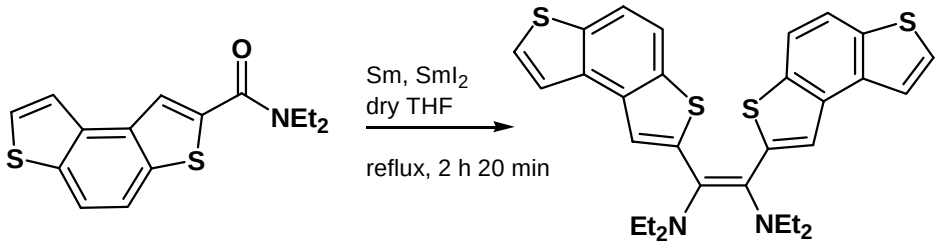
Scheme 11. Reaction of the anion of the benzodithiophene with diethylcarbamoyl chloride

The alternative reaction sequence, reported in Scheme 12, even if including a higher number of steps, proved to be definitely more efficient and furnished amide **29** in about 73**%** overall yield starting from the benzodithiophene **23**. In detail, **23** was transformed into the 2-ethoxycarbonyl derivative **32** by treatment of the monoanion, generated with *n*-BuLi at –78 °C, with $ClCO_2Et$. Beside the expected ester **32**, a small amount (14%) of the diester **33** was also isolated. Ester **32** was then hydrolyzed to give the carboxylic acid **34** in quantitative yield and, the in situ formed acyl chloride, was reacted with diethylamine to furnish the desired amide **29**, as yellow-green oil in 99% yield.



Scheme 12. Synthesis of *N*,*N*-di-ethyl-benzodithien-2'-yl carboxyamide **29**

Amide **29** was then submitted to the Sm/SmI_2 mediated coupling. (Scheme 13) From the reaction we isolated the disubstituted alkene **28**, in 35% yield, as single isomer for which we could not assign the configuration.

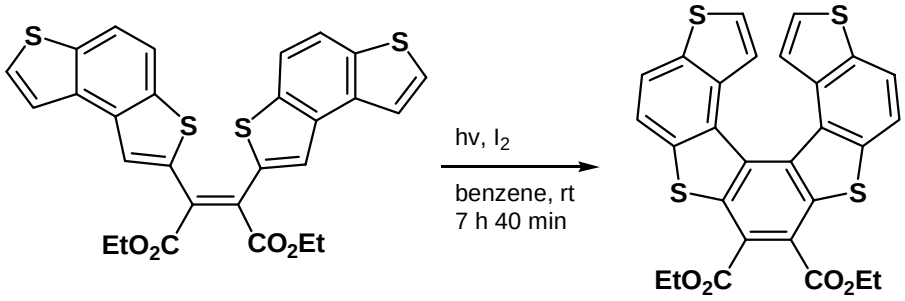


29 **28**, 35%

Scheme 13. Synthesis of 1,2-*N*,*N*,*N*,*N*-tetra-ethyl-bis-amine-1,2-bis(benzodithien-2'-yl)ethene **28**

Photocyclization of alkenes 20, 21 and 28 to the corresponding helicenes

Alkenes **20**, **21** and **28** are direct precursors of the corresponding helicenes substituted in the positions 7 and 8, in principle obtainable through photochemical cyclization of the above mentioned alkenes. No examples of photocyclization are reported on 1,2-(bis-benzodithienyl)ethenes substituted with ester, trifluoromethyl and dialkylamino groups. We therefore submitted them to the photochemical conditions usually utilized for the conversion of 1,2-(bis-benzodithienyl)ethenes into helicenes. In particular, a 75:25 *E*/*Z* mixture of the alkene **20** was irradiated with a 125 Watt medium pressure Hg lamp, in benzene solution and in the presence of a catalytic amount of iodine, for 8 hours; from the reaction we isolated the corresponding helicene **6** in 50% yield as an orange solid. (Scheme 14)



20
d.r. 75:25

6, 50%

Scheme 14. Synthesis of 7,8-di-ethoxycarbonyl-tetrathia-[7]-helicene **6**

Compound **6** is the first example of a helicene substituted in the 7,8 positions with two electron-withdrawing groups, and is interesting because it has the 2,13 positions free for further functionalization.

Also in view of a deeper investigation of linear and non-linear optical properties, we examined the

UV-Vis spectra of helicenes **5**, **6** and **7** in diluted CH_2Cl_2 solution and we compared them with the parent helicene **1** and helicene **16** which have no electron-withdrawing substituents (Figure 2). It can be clearly noticed how the shape and wavelength of the UV absorption changes according to the different extension of the π-conjugated system of helicenes. As expected, helicenes **5**, **6** and **7** show a red shift (427, 410 and 413 nm respectively) compared to helicenes **1** and **16** (387 and 390 nm): this can be attributed to the presence, on the helical system of **5-7**, of two acrylic, methoxycarbonyl, and trifluoromethyl electron-acceptor moieties. In the case of helicene **5**, the presence of the double bond between the helicene and ester group brings to an extension of the π-conjugated system, and to a more pronounced red shift (i.e., 427 nm for **5** and 410 nm for **6**).

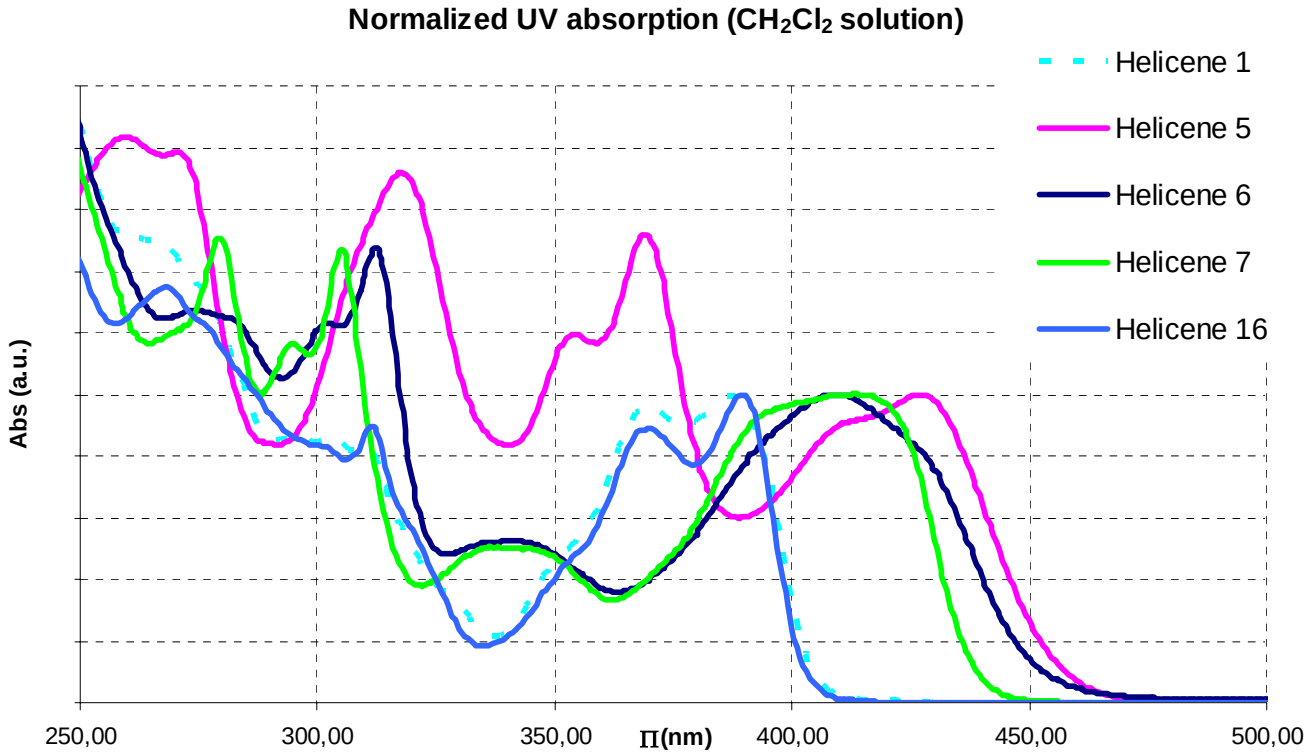
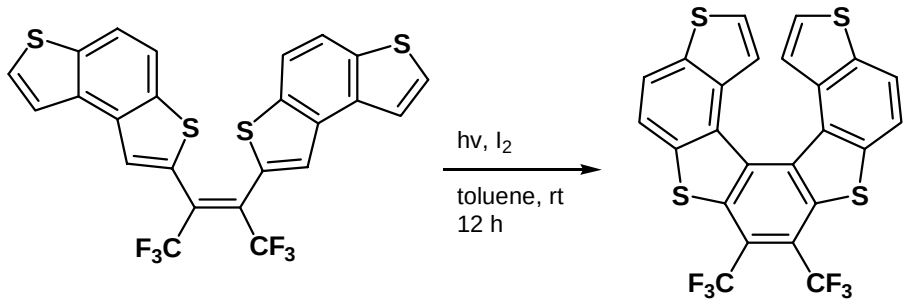


Figure 2. UV absorptions of the helicenes **1**, **5-7** and **16** in CH_2Cl_2 solution. The data of each helicene have been normalized for a better clarity

The photocyclization of **21**, performed with a medium pressure Hg lamp in the same conditions used for the synthesis of helicene **6**, afforded the corresponding helicene **7** in 70% yield as a white solid, which was completely characterized by analytical and spectroscopic data. (Scheme 15) Helicene **7** not only has two powerful electron-withdrawing groups in the 7,8 p osition, but is the first example of trifluoromethyl substituted helicene.

We were not able to find appropriate conditions to obtain the corresponding helicene from alkene **28**. In

fact, when **28** was submitted to irradiation with an Hg medium pressure 150watt lamp for 15 min, it did not cyclise to helicene and the only compound recovered was amide **29**.



21
d.r. 65:35

7, 70**%**

Scheme 15. Synthesis of 7, 8-di(trifluoromethyl)helicene **7**

This result could be attributed to a tendency of the electron-rich double bond present in alkene **28** to be oxidized in the photochemical conditions. Therefore, for the moment, it is not possible to obtain tetrathiahelicenes substituted with electron-donor groups in such positions.

CONCLUSIONS

In this paper we have described the preparation of new functionalized tetrathia[7]helicenes utilizing two complementary methodologies. The first one is based on the direct functionalization of the helical system through the formation of mono- or dianions at the terminal thiophene rings, and reaction with electrophilic reagents. This strategy allows the preparation of tetrathia[7]helicenes substituted in 2,13 positions with electron donor and electron acceptors groups. The effect of some of these substituents on the helicene π-conjugated system is shown by UV-Vis spectra.

The second strategy is based on the synthesis of appropriately substituted 1,2-(bis-benzodithienyl)ethenes from which, the corresponding helicenes **6** and **7** are obtained by photocyclization. By this route it was possible to synthesise helicenes substituted in the 7,8 positions, that is in the central arene ring, with electron-acceptor groups. The possibility of making available tetrathiahelicenes decorated with several, different substituents is of great importance to monitor their electronic properties in order to find the best candidates in view of potential applications in material science and catalysis. In principle, the two methodologies described in this paper can give access to a large number of differently substituted thiahelicenes. Studies to prepare optically active heterohelicenes in order to evaluate their NLO properties, and to insert them in polymeric materials, are under way in our laboratory.

EXPERIMENTAL

General. Reagents obtained from commercial sources were used without further purification. Benzodithiophene **23**[15] and helicene **16**[5b] were prepared according to the literature. THF was dried by distillation over sodium wires/benzophenone, and the *n*-BuLi solutions in hexane were titrated. Unless otherwise stated, all reactions were performed under an inert atmosphere, after the glassware had been flame-dried. In order to monitor the progress of the reactions, TLC was performed using Merck silica gel 60 F254 precoated plates. Flash chromatography was performed using Merck silica gel 60, 230-400 mesh. Melting points were determined by means of a Büchi B 540 apparatus and are uncorrected. IR spectra were recorded on a PerkinElmer FT-IR 1725X spectrometer and only noteworthy absorptions are listed. UV spectra were recorded with a PerkinElmer Lambda E2 210 spectrophotometer. Mass spectra were recorded on LCQ Advantage Thermo equipped with ion trap and APCI source on 50-2000 *m/z* range. High-resolution mass spectra were recorded on a Vg Analytical 7070 EQ spectrometer. ^{1}H NMR (300 MHz and 200 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282.4 MHz) spectra were recorded on Bruker AC 300, Bruker AC 200, and Bruker AMX 300 spectrometers. DSC analysis were performed on Mettler Toledo DSC823^{e}. Elemental analysis were performed using a Perkin Elmer 2400 Series II, CHNS/O Analyzer.

Synthesis of *N*-[(7,8-di-*n*-Pr-tetrathia[7]helicen-2-yl methyl)ethane-1,2 diamine 2

To a solution of {2-[(7,8-dipropylthiahelicen-2-yl-methyl)-amino]ethyl}carbammic acid *tert*-butyl ester **9** (0.029 g, 0.044 mmol) in CH_2Cl_2 (1 mL), TFA (1 mL) was added at rt, under nitrogen atmosphere. The red reaction mixture was stirred for 1 h then evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (3 mL) and washed with aqueous NaOH (2 M, 2 x 3 mL). The collected aqueous phases were extracted with CH_2Cl_2 (3 x 5 mL), the combined organic phases were washed with H_2O, dried over Na_2SO_4, filtered end evaporated under vacuum. The residue was washed with pentane (2 × 3 mL) and isolated as pale yellow solid (16 mg, 65% yield); DSC, onset 210 °C, peak 225 °C. IR (Nujol, cm^{-1}): 3391, 1651, 1540, 1128. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, 6 H, CH_3CH_2, *J* = 7.3 Hz), 1.79-1.93 (m, 4 H, CH_2CH_3), 2.1-2.4 (bs, 3 H, NH_2 + NH), 2.46 (t, 2 H, CH_2CH_2, *J* = 5.7 Hz), 2.74 (t, 2 H, CH_2CH_2, *J* = 5.7 Hz), 3.07-3.18 (m, 4 H, CH_2Ar), 3.50 (d, 1 H, CH_2NH, *J* = 14.4 Hz), 3.55 (d, 1 H, CH_2NH, *J* = 14.4 Hz), 6.58 (s, 1 H, CH, thiophene), 6.78 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.92 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.86-7.9 (m, 2 H, CH, Ph), 7.94 (d, 1 H, CH, Ph, *J* = 8.5 Hz), 7.99 (d, 1 H, CH, Ph, *J* = 8.5 Hz,). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (CH_3), 23.3 (CH_2), 34.4 (CH_2), 41.4 (CH_2), 48.3 (CH_2), 118.2 (CH), 118.9 (CH), 120.7 (CH), 123.3 (CH), 123.8 (CH), 125.6 (CH), 128.1 (C_q), 131.2-131.6 (C_q), 132.2-132.3 (C_q), 136-136.2 (C_q), 139.7 (C_q), 143.2 (C_q). MS (EI^{+}): *m/z* (%) = 456 (55), 499 (100), 515 (60), 558 (35) $[M]^{+}$. HRMS-EI^{+}: *m/z* calculated for $C_{31}H_{30}N_2S_4$: 558.129186; found: 558.128600 $[M]^{+}$. ***Anal.*** Calcd for $C_{31}H_{30}N_2S_4$: C, 66.63; H, 5.41; N, 5.01. Found: C, 66.24; H, 5.92; N, 5.31. UV/Vis (CH_2Cl_2): λ_{max} = 314,

374, 394 nm.

***N*-(2-Aminoethyl)-7',8'-dipropyltetrathia[7]helicene-2'-yl-1-carboxyamide 3 from the helicene 10**

To ethylenediamine (2 mL) a solution of helicene ethyl ester **10** (0.17 g, 0.30 mmol) in CH_2Cl_2 (1 mL) was dropped at 50 °C under a nitrogen atmosphere. After 2 h ethylenediamine was distilled under vacuum and the orange residue was diluted with H_2O (10 mL) and CH_2Cl_2 (30 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The solid residue was washed with pentane (40 mL) to remove the starting material **10** (20 mg, 12%), then the residue was dissolved in CH_2Cl_2 (20 mL) and washed with an aqueous solution of HCl (4,5 M, 25 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL) and the collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The product **3** was recovered as hydrochloride salt (120 mg, 64% yield) as pale yellow solid. R_f = 0.2 (AcOEt-MeOH = 8:2); mp 185-190 °C; IR (KBr, cm^{-1}): 3402, 2957-2867, 2027, 1634, 1529, 1455, 1384, 1326-1278, 1162, 1093. ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 1.10 (t, 6 H, CH_3, *J* = 7.15 Hz), 1.70-1.90 (m, 4 H, CH_2), 2.60-2.80 (m, 1 H, CH_2), 3.00-3.60 (m, 7 H, CH_2), 6.45 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.17 (s, 1 H, CH, thiophene), 7.23 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.98-8.00 (bs, 4 H, NH_3 + NH), 8.18-8.30 (m, 4 H, CH, Ph). ^{13}C NMR (75 MHz, DMSO-*d6*/D_2O): δ =15.0 (CH_3), 23.6 (CH_2), 34.3 (CH_2), 37.1 (CH_2), 120.0 (CH), 122.0 (CH), 122.1 (CH), 124.4 (CH), 126.0 (CH), 127.2 (CH), 127.6 (C_q), 128.0 (C_q), 130.9 (C_q), 131.6 (C_q), 132.9 (C_q), 133.4 (C_q), 135.1 (C_q), 135.5 (C_q), 136.4 (C_q), 136.6 (C_q), 136.7 (C_q), 137.2 (C_q), 138.4 (C_q), 139.9 (C_q), 140.1 (C_q), 162.9 (C_q). MS (EI^+): *m/z* (%) = 514 (40), 529 (25), 543 (10), 554 (100), 572 (35) $[M]^+$. HRMS-EI^+: *m/z* calculated for $C_{31}H_{28}N_2OS_4$: 572.108451; found: 572.104920 $[M]^+$. *Anal.* Calcd for $C_{31}H_{29}ClN_2OS_4$: C, 61.11; H, 4.80; N, 4.60. Found: C, 60.96; H, 5.09; N, 4.81. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 402 (4.16), 363 (4.06), 268 (4.84), 249 nm (4.79).

***N*-(2-Aminoethyl)-7',8'-di-*n*-Pr-tetrathia[7]helicene-2'-yl-1-carboxyamide 3 from the helicene 14**

TFA (692 µL, 9,32 mmol) was added to a solution of the helicene **14** (0.157 g, 0.23 mmol) in dry CH_2Cl_2 (2 mL), under a nitrogen atmosphere. The solution was stirred at rt for 1 h then the solvent was evaporated under vacuum. The residue was washed with pentane, filtered to give the product **3** as trifluoroacetic salt (126 mg, 80% yield) as pale yellow solid. R_f = 0.2 (AcOEt-MeOH = 8:2); mp 218-220 °C. IR (KBr, cm^{-1}): 3412, 3051-2868, 1677-1640, 1529, 1309-1278, 1203-1137. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.11-1.16 (m, 6 H, CH_3), 1.80-1.90 (m, 4 H, CH_2), 2.60-2.90 (m, 2 H), 3.00-3.30 (m, 6 H), 6.47 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.18 (s, 1 H, CH, thiophene), 7.25 (d, 1 H, CH, thiophene, *J* = 5.5 Hz); 7.71 (bs, 3 H, NH_3); 7.94 (bt, 1 H, NH); 8.22-8.30 (m, 3 H, CH), 8.32 (d, 1 H, CH,

Ph, J = 8.6 Hz). ^{13}C NMR (75 MHz, DMSO-d_6/D_2O): δ = 14.4 (CH_3), 23.0 (CH_2), 33.8 (CH_2), 36.4 (CH_2), 38.2 (CH_2), 119.3 (CH), 121.2 (CH), 121.6 (CH), 123.9 (CH), 125.6 (CH), 126.2 (CH), 127.1 (C_q), 127.5 (C_q), 130.4 (C_q), 131.1 (C_q), 132.2 (C_q), 132.6 (C_q), 134.6 (C_q), 134.9 (C_q), 135.8 (C_q), 135.9 (C_q), 136.7 (C_q), 136.8 (C_q), 137.8 (C_q), 139.1 (C_q), 139.4 (C_q), 161.8 (C_q). ^{19}F NMR (282.4 MHz, DMSO-d_6/D_2O): -73.6. ^{19}F NMR (282.4 MHz, $CDCl_3$): -76.1. MS (EI^+): *m/z* (%) = 554 (100), 668 (20), 573 $[M]^+$ (10). HRMS-EI^+: *m/z* calculated for $C_{31}H_{29}N_2O_1S_4$: 573.11572; found: 573.11462 $[M]^+$; calculated for $C_{31}H_{28}N_2O_1S_4Na$: 595.09767; found: 595.09667 $[M+Na]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 404 (4.2), 364 (4.1), 268 (4.8), 248 nm (4.8).

_N_-(2-Aminoethyl)tetrathia[7]helicene-2'-yl-1-carboxyamide 4

*Starting from N-(2-Boc-amino-ethyl)tetrathia-[7]-helicene-2'-yl-1-carboxyamide **15***:

To a solution of tetrathiahelicene **15** (0.035 g, 0.059 mmol) in CH_2Cl_2 (1 mL), TFA (150 μL, 2.05 mmol) was added under a nitrogen atmosphere. The solution was stirred 1 h at rt. The solution was evaporated under vacuum then diluted with CH_2Cl_2 (5 mL) and washed with NaOH (1 M; 5 mL). After separation, the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL), then the collected organic phases were washed with a saturated solution of NaCl (5 mL), dried over Na_2SO_4, filtered and evaporated under vacuum. The product **4** with the free amino function was washed with pentane and recovered as yellow solid (19.3 mg, 67% yield).

*Starting from tetrathiahelicene-2-ethyl carboxylate **11**:*

Under a nitrogen atmosphere, a solution of tetrathiahelicene **11** (0.051 g, 0.107 mmol) in CH_2Cl_2 (1 mL) was added in 20 min in ethylenediamine (2 mL) heated at 50 °C. After 1 h the ethylendiamine was distilled under vacuum, the residue was diluted with *n*-BuOH (5 mL) and redistilled. The residue was washed with CH_2Cl_2 (2 mL) and MeOH (2 mL) obtaining the product **4** with the free amino function as yellow solid (35.5 mg, 68% yield); DSC, onset 143.4 °C, peak 150.4 °C. IR (Nujol, cm^{-1}): 3290, 1645, 1540, 1297, 1148. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.74-2.78 (t, 2 H, CH_2, J = 5.8 Hz), 3.06-3.14 (m, 1 H, CH_2), 3.30-3.40 (m, 1 H, CH_2), 5.32 (bs, 1 H, NH), 6.70 (d, 1 H, CH, thiophene, J = 5.5 Hz), 6.98 (d, 1 H, CH, thiophene, J = 5.5 Hz), 6.99 (s, 1 H, CH, thiophene), 7.95-8.08 (m, 6 H CH, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.4 (CH_2), 42.8 (CH_2), 119.2 (CH), 120.7 (CH), 121.1 (CH), 121.4 (CH), 124.8 (CH), 125.0 (CH), 125.2 (CH), 129.5 (C_q), 130.4 (C_q), 131.0 (C_q), 134.9 (C_q), 135.9 (C_q), 136.1 (C_q), 136.5 (C_q), 137.1 (C_q), 137.3 (C_q), 137.7 (C_q), 137.9 (C_q), 138.3 (C_q), 162.5 (C_q). MS (EI^+): *m/z* (%) = 368 (90), 400 (50), 430 (90), 445 (65), 470 (100), 488 (40) $[M]^+$. HRMS-EI^+: *m/z* calculated for $C_{25}H_{16}N_2OS_4$: 488.014550; found: 488.014560 $[M]^+$. *Anal.* Calcd for $C_{25}H_{16}N_2OS_4$: C, 61.45; H, 3.30; N, 5.73. Found: C, 62.01; H, 3.42; N, 5.46.

Synthesis of (*E*/*E*)-7,8-di-*n*-Pr-2,13-di-vinylcarboxymethyltetrathia[7]helicene 5

Under a nitrogen atmosphere, diiodohelicene **17** (73,0 mg; 0,10 mmol; 1 eq), $Pd(OAc)_2$ (2,2 mg; 0,01 mmol; 0,1 eq), AcONa (32,4 mg; 0,39 mmol; 4 eq), and Bu_4NBr (88,8 mg; 0,39 mmol; 4 eq) were dissolved in DMF (4 mL). After 10 min stirring at rt, methyl acrylate (53,4 µL, d = 0,955 g/mL; 0,30 mmol; 3 eq) was dropped to the solution, then the reaction was heated at 120 °C for 20 min. At rt, the course of the reaction was monitored by TLC (hexane/AcOEt = 8:2) then the mixture was diluted with H_2O (20 mL) and AcOEt (20 mL). The phases were separated, the organic phase was washed with H_2O (25 mL), the collected aqueous phases were extracted with AcOEt (30 mL) and the collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (with a gradient from hexane/AcOEt = 9:1 to 8:2) to yield pure product **5** (62 mg, 94% yield) as yellow solid and the monosubstituted helicene **18** (2 mg, 4% yield).

7,8-di-*n*-Pr-2,13-divinylcarboxymethyltetrathia[7]helicene 5

R_f = 0,24 (hexane/AcOEt = 8:2); mp 209-211 °C. IR (Nujol, cm^{-1}): 1717, 1621. ^{1}H-NMR (300 MHz, $CDCl_3$,): δ 1.16 (t, 6 H, CH_3, *J* = 7.3 Hz), 1.80-1.94 (m, 4 H, CH_2), 3.02-3.21 (m, 4 H, CH_2), 3.73 (s, 6 H, OCH_3), 5.97 (d, 2 H, CH=, *J* = 15.6 Hz), 6.80 (s, 2 H, CH, thiophene), 7.17 (d, 2 H, CH=, *J* = 15.6 Hz), 7.92 (d, 2 H, CH, Ph, *J* = 8.5 Hz), 8.00 (d, 2 H, CH, Ph, *J* = 8.5 Hz). ^{13}C (75 MHz, $CDCL_3$): δ 14.7 (CH_3), 23.3 (CH_2), 34.4 (CH_2-Ph), 51.6 (OCH_3), 118.4 (CH), 120.6 (CH), 120.7 (CH), 127.7 (C_q), 129.4 (CH), 131.1 (C_q), 132.7 (C_q), 135.4 (C_q), 136.6 (C_q), 137.2 (CH), 137.4 (C_q), 137.5 (C_q), 140.2 (C_q), 166.8 (C_q). MS (ESI^+): *m/z* = 677 $[M + Na]^+$, 1331 $[2M + Na]^+$, 1987 $[3M + Na]^+$. HRMS (ESI^+): *m/z* calculated for $C_{36}H_{30}O_4S_4Na$: 677.09191, found: 677.08935 $[M+Na]^+$. ***Anal.*** Calcd for $C_{36}H_{30}O_4S_4$: C, 66.03; H, 4.62. Found. C, 66.37; H, 4.89. UV-Vis (CH_2Cl_2): λ_{max} (log ε): 427.0 (4.49), 369.0 (4.67), 317.5 (4.73), 259.5 (4.75), 232.5 nm (4.70).

7,8-di-*n*-Pr-2-vinylcarboxymethyltetrathia[7]helicene 18

R_f = 0,42 (hexane/AcOEt = 8:2). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.12-1.18 (m, 6 H, CH_3), 1.80-1.90 (m, 4 H, CH_2), 3.03-3.20 (m, 4 H, CH_2Ph), 3.73 (s, 3 H, OCH_3), 5.96 (d, 1 H, CH=, *J* = 15.6 Hz), 6.71 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.84 (s, 1 H, CH, thiophene), 6.95 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.14 (d, 1 H, CH=, *J* = 15.6 Hz), 7.88 (d, 1 H, CH, Ph, *J* = 8.5 Hz), 7.90 - 8.0 (m, 2 H, CH, Ph), 8.04 (d, 1 H, CH, Ph, *J* = 8.5 Hz). MS (EI^+): *m/z* (%) = 570 $[M]^+$ (100), 541 (5). HRMS (EI^+): *m/z* calculated for $C_{32}H_{26}O_2S_4$: 570.081568, found: 570.080575 $[M]^+$.

Synthesis of 7,8-Bis(ethoxycarbonyl)tetrathia[7]helicene 6

A solution 6×10^{-4} M of 1,2-di-(ethoxycarbonyl)-1,2-di-(benzodithien-2'-yl)-ethene **20** (70 mg, 0.13 mmol, as mixture of two isomers) in benzene (220 mL) with a catalytic amount of iodine was irradiated at

rt using a 125-W unfiltered medium pressure Hg lamp, equipped with a quartz jacket. After 7 h 40 min of irradiation, the toluene was evaporated under vacuum and the residue was purified by column chromatography on silica gel (eluent: with a gradient from hexane/AcOEt = 9:1 to AcOEt) to yield helicene **6** as orange solid (36 mg, 50% yield) and starting material **20** (11 mg, 15% yield); mp 144-148 °C. IR (Nujol, cm^{-1}) = 1713. ^1H (200 MHz, $CDCl_3$) δ = 1.50 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.58 (q, 4 H, CH_2, *J* = 7.1 Hz), 6.55 (d, 2 H, CH, thiophene, *J*= 5.5 Hz), 6.92 (d, 2 H, CH, thiophene, *J* = 5.5 Hz), 8.00 (d, 2 H, CH, Ph, *J* = 8.5 Hz), 8.10 (d, 2 H, CH, Ph, *J* = 8.5 Hz). ^{13}C (75 MHz, DMSO-*d6*) δ = 14.2 (CH_3), 62.4 (CH_2), 118.2 (CH), 122.6 (CH), 123.6 (C_q), 124.8 (CH), 125.0 (CH), 129.2 (C_q), 132.2 (C_q), 135.9 (C_q), 136.7 (C_q), 137.5 (C_q), 139.2 (C_q), 166.7 (C_q). MS (ESI^+): *m/z*= 569 $[M+Na]^+$, 1115.0 $[2M+Na]^+$. HRMS (ESI^+): *m/z* calculated for $C_{28}H_{18}S_4O_4Na$: 568.99801, found: 568.99635 $[M]^+$; calculated for $C_{56}H_{36}S_8O_8Na$: 1115.00680 found: 1115.00425 $[M+Na]^+$. *Anal.* Calcd for $C_{28}H_{18}S_4O_4$: C, 61.51; H, 3.32. Found: C, 60.38; H, 3.89. UV/Vis (CH_2Cl_2): λ_{max} (log ε)=410 (4.21), 345 (3.93), 312 (4.38), 305 (4.30), 275 nm (4.32).

Synthesis of 7,8-Bis(tri-fluoromethyl)tetrathia[7]helicene 7

A yellow solution of 1,1,1,4,4,4-hexafluoro-2,3-di-[2'-benzodithiophenyl]-but-2-ene **21** (6.8×10^{-4} M, 92 mg, 0,17 mmol, 65:35 mixture of two isomers) with iodine (43 mg, 0.17 mmol) in toluene (250 mL) was irradiated at rt using a 125-W unfiltered medium pressure Hg lamp, equipped with a quartz jacket. After 12 h of irradiation, the toluene was evaporated under vacuum and the residue was purified by column chromatography on silica gel (eluent: with a gradient from hexane/AcOEt = 95:5 to 7:3; then AcOEt). The helicene **7** was recovered after washing with pentane as light yellow solid (30 mg, 70% yield). R_f = 0.6 (hexane/ AcOEt = 95:5); mp 272-275 °C. IR (film, cm^{-1}) = 1242, 1157-1135, 707. ^1H (300 MHz, $CDCl_3$): δ = 6.37 (d, 2 H, CH, thiophene, *J* = 5.6 Hz), 6.90 (d, 2 H, CH, thiophene, *J* = 5.6 Hz), 7.97 (d, 2 H, CH, Ph, *J* = 8.6 Hz), 8.10 (d, 2 H, CH, thiophene, *J* = 8.6 Hz). ^{13}C (75 MHz, $CDCl_3$): δ = 117.7 (CH), 121.9 (C_q), 123.5 (CH), 124.4 (CH), 125.6 (C_q), 125.9 (CH), 128.5 (C_q), 133.4 (C_q), 135.8 (C_q), 136.2 (C_q), 137.1 (C_q), 138.6 (C_q). ^{19}F (282.4 MHz, $CDCl_3$): δ = -54.82 (s). MS (ESI^+): *m/z* = 561 $[M+Na]^+$. HRMS (ESI^+): *m/z* calculated for $C_{24}H_7F_6S_4Na$: 560.93052, found: 560.93206 $[M+Na]^+$. *Anal.* Calcd for $C_{24}H_7F_6S_4$: C, 53.52; H, 1.50. Found: C, 53.0; H, 1.79. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 413 (4.23), 338 (3.93), 305 (4.40), 290 (4.29), 280 (4.41), 238 nm (4.64).

Synthesis of {2-[(7,8-di-*n*-Pr-tetrathia[7]helicen-2-ylmethyl)amino]ethyl}carbammic acid *tert*-butyl ester 9

To a solution of 7,8-dipropyl-2-carboxyaldehyde thiahelicene **8** (0.083 g, 0.161 mmol) in CH_2Cl_2 (4.5 mL) a solution of (2-aminoethyl)-carbamic acid *tert*-butyl ester (0.078 g, 0.484 mmol) in dry MeOH (2.5

mL) was added under nitrogen atmosphere. At rt a mixture of $ZnCl_2$ (0.037 g, 0.274 mmol) and $NaCNBH_3$ (0.034 g, 0.549 mmol) in dry MeOH (2 mL) was added dropwise and the orange solution was stirred at rt for 18 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with a saturated solution of NaCl (15 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL) and the collected organic phases were dried over Na_2SO_4, filtered on celite and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (with a gradient from hexane to hexane-AcOEt = 1:1) to give compound **9** (79 mg, 80% yield) as pale yellow solid. R_f = 0.4 (hexane-AcOEt = 1:1); mp 185-188 °C. IR (Nujol, cm^{-1}): 3428, 1714. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, 6 H, CH_3, *J* = 7.3 Hz), 1.48 (s, 9 H, *t*Bu), 1.82-1.93 (m, 4 H, CH_2CH_3), 2.44-2.50 (m, 2 H, CH_2NH), 3.04-3.21 (m, 6 H, CH_2Ar + CH_2NHBoc), 3.45 (d, 1 H, CH_2, *J* = 14.4 Hz), 3.53 (d, 1 H, CH_2, *J* = 14.4 Hz), 4.89 (bd, 1 H, NH), 6.56 (s, 1 H, CH, thiophene), 6.77 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.91 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.86-7.90 (m, 2 H, CH, Ph), 7.94 (d, 1 H, CH, Ph, *J* = 8.5 Hz), 7.99 (d, 1 H, CH, Ph, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (CH_3), 23.3 (CH_2), 28.5 (CH_3), 34.4 (CH_2), 48.1 (CH_2), 48.2 (CH_2), 79.2 (C_q), 118.3 (CH), 118.9 (CH), 120.7 (CH), 123.5 (CH), 123.8 (CH), 125.7 (CH), 128.1 (C_q), 131.2 (C_q), 131.6 (C_q), 132.2 (C_q), 132.3 (C_q), 135.9-136.3 (C_q), 139.7 (C_q), 142.7 (C_q), 156.1 (C_q). MS (EI^+): *m/z* (%) 456 (55), 499 (100), 515 (45), 584 (80), 601 (40), 658 (20) $[M]^+$. HRMS-EI^+: *m/z* calculated for $C_{36}H_{38}N_2O_2S_4$: 658.181616; found: 658.180730 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 245 (4.70), 269 (4.54), 314 (4.39), 374 (4.47), 394 nm (4.46).

Synthesis of [Tetrathia[7]helicen-2-yl]ethyl carboxylate 11

To a solution of tetrathiahelicene **1** (0.1 g, 0.256 mmol) in dry THF (7 mL), *n*-BuLi (1.54 M in hexane, 0.18 mL, 0.27 mmol) was added at –78 °C under nitrogen atmosphere. The solution was stirred 5 min at –78 °C then 15 min at rt. The solution was cooled at –78 °C and ethyl chloroformate (262 μL, 0.27 mmol) was added. The mixture was stirred at –78 °C for 30 min then, at rt, the solution was quenched with a saturated solution of $NaHCO_3$ (15 mL) and diluted with CH_2Cl_2 (15 mL). After separation, the aqueous phase was extracted with CH_2Cl_2 (2 × 15 mL), then the collected organic phases were dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by flash chromatography on silica gel (with a gradient from hexane to hexane/AcOEt = 7:3) to give compound **11** (91 mg, 75% yield) as yellow-orange solid and recovering 23% of helicene **1** as starting material (23 mg). R_f = 0.23 (hexane/AcOEt = 7:3); mp>250 °C. IR (Nujol, cm^{-1}): 1699, 1277, 1148, 1060. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.19 (m, 3 H, CH_3), 4.02-4.08 (m, 1 H, CH_2), 4.2-4.3 (m, 1 H, CH_2), 6.67 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.96 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.39 (s, 1 H, CH, thiophene), 7.97-8.10 (m, 6 H, CH, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 61.0 (CH_2), 118.6 (CH), 120.3 (CH), 120.7 (CH), 121.1 (CH), 121.4 (CH), 124.6 (CH), 124.9 (CH), 129.5 (C_q), 129.9 (C_q), 130.4 (C_q), 131.3

(CH), 131.6 (C_q), 135.0 (C_q), 135.6 (C_q), 136.8 (C_q), 137.1 (C_q), 137.7 (C_q), 137.9 (C_q), 139.4 (C_q), 163.0 (C_q). MS (EI^+): *m/z* (%) = 355 (20), 368 (35), 402 (20), 474 (100) $[M]^+$. HRMS-EI^+: *m/z* calculated for $C_{25}H_{14}O_2S_4$: 473.987667; found: 473.986630 $[M]^+$.

7,8-di-*n*-Pr-tetrathia[7]helicen-2-ylcarboxylic acid 12

To a yellow suspension of helicene **10** (0.29 g, 0.52 mmol) in MeOH (10 mL) and H_2O (4 mL), KOH (1 g, 17.86 mmol) was added at rt. After 10 min the yellow solution was evaporated under vacuum, the oily residue was dissolved with CH_2Cl_2 (25 mL) and diluted with H_2O (10 mL). The phases were separated and the organic phase was washed with an aqueous solution of HCl (30%, 20 mL). The phases were separated and the organic phase was dried over Na_2SO_4, filtered over celite then the solvent was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (5 mL) then precipitated with hexane and filtered to give the product **12** (234 mg, 85% yield) as yellow solid. DSC 150-180 °C, exotherm peak; IR (KBr, cm^{-1}): 3436, 2958-2868, 1700-1640, 1159. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.10 (t, 6 H, CH_3, *J* = 7.27 Hz), 1.70-1.90 (m, 4 H, CH_2), 3.0-3.15 (m, 4 H, CH_2 Ph), 6.53 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.18 (d, 1 H, CH, thiophene), 7.30 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 8.19 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 8.23-8.27 (m, 2 H, CH, Ph), 8.34 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 12.85 (bs, 1 H, OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.3 (CH_3), 22.8 (CH_2), 33.7 (CH_2), 118.8 (CH), 121.5 (CH), 121.7 (CH), 123.7 (CH), 125.9 (CH), 126.9 (C_q), 127.2 (C_q), 129.7 (C_q), 130.0 (C_q), 131.1 (C_q), 132.0 (C_q), 132.4 (C_q), 134.3 (C_q), 134.8 (C_q), 135.4 (C_q), 135.9 (C_q), 136.8 (C_q), 138.8 (C_q), 139.1 (C_q), 139.4 (C_q), 162.8 (C_q). MS (EI^+): *m/z* (%) = 486 (30), 530 (100) $[M]^+$. HRMS-EI^+: *m/z* calculated for $C_{29}H_{22}O_2S_4$: 530.050269; found: 530.050540 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 401 (4.26), 334 (4.32), 294 (4.51), 265 (4.62), 245 nm (4.70).

Synthesis of 2-Tetrathia[7]helicenecarboxylic acid 13

To solution of tetrathiahelicene ethyl ester **11** (87 mg, 0.183 mmol) in MeOH (6 mL) and H_2O (1 mL), KOH (1 g, 17.8 mmol) was added at room temperature. The yellow suspension was heated at 50 °C for 15 min and the yellow solution was acidified with HCl (10 N; until pH =1) and diluted with CH_2Cl_2 (40 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (4 x 40 mL), the collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The product **13** was isolated (68 mg, 83% yield) as yellow solid. DSC, onset 105.6 °C, peak 109.6 °C; IR (Nujol, cm^{-1}): 3600, 1710-1667, 1157. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.68 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.90 (s, 1 H, CH, thiophene), 7.28 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 8.10 (d, 1 H, CH, Ph, *J* = 8.6 Hz), 8.16 (d, 1 H, CH, Ph, *J* = 8.6 Hz), 8.18 (d, 1 H, CH, Ph, *J* = 8.6 Hz), 8.22 (d, 1 H, CH, Ph, *J* = 8.6 Hz), 8.24-8.30 (m, 2 H, CH, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.3 (CH), 119.7 (CH), 121.2 (CH),

121.3 (CH), 122.4 (CH), 122.5 (CH), 124.5 (CH), 125.1 (CH), 126.2 (CH), 129.6 (C_q), 129.7 (C_q), 130.6 (C_q), 130.9 (C_q), 135.9 (C_q), 136.3 (C_q), 136.6 (C_q), 136.7 (C_q), 137.7 (C_q), 137.6 (C_q), 138.3 (C_q), 165.5 (C_q). MS (APCI$^-$): *m/z* (%) = 401 (25), 445 (100) $[M]^-$. HRMS-EI$^+$: *m/z* calculated for $C_{23}H_{10}O_2S_4$: 445.956367; found: 445.962400 $[M]^+$.

_N_-(2-Boc-aminoethyl)-7',8'-di-_n_-Pr-tetrathia[7]helicene-2'-yl-1-carboxyamide 14

A solution of helicene **12** (0.22 g, 0.41 mmol) in $SOCl_2$ (3 mL) was heated at 50 °C for 1 h under a nitrogen atmosphere, then the solvent was distilled under vacuum. The acyl chloride was dissolved in dry THF (1 mL), then DIPEA (216 μL, 1.26 mmol) and a solution of *N*-Boc-ethylenediamine (0.074 g, 0.46 mmol) in dry THF (2 mL) were dropped. The mixture was heated at 50 °C for 2 h then the reaction was quenched with a saturated solution of $NaHCO_3$ (5 mL) and diluted with CH_2Cl_2 (20 mL). The phases were separated, the aqueous phase was extracted with CH_2Cl_2 (2 × 7 mL) and the collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The residue was purified with flash chromatography on silica gel (hexane-AcOEt = 6:4) to give the product **14** (209 mg, 76% yield) as yellow solid. R_f = 0.3 (hexane-AcOEt = 6:4); DSC, onset 200, peak 243 °C. IR (KBr, cm^{-1}): 3427, 2958 - 2868, 1700, 1639, 1525-1454, 1162. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, 3 H, CH_3, *J* = 7.3 Hz), 1.16 (t, 3 H, CH_3, *J* = 7.3 Hz), 1.46 (s, 9 H, *t*Bu), 1.80-1.90 (m, 4 H, CH_2), 3.10-3.50 (m, 8 H, CH_2), 4.8 (bs, 1 H, NH), 5.3 (bs, 1 H, NH), 6.71 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.97 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.02 (s, 1 H, CH, thiophene), 7.95 (d, 1H, CH, Ph, *J* = 8.5 Hz), 8.01 (d, 1 H, CH, Ph, *J* = 8.5 Hz), 8.04 (d, 1 H, CH, Ph, *J* = 8.5 Hz), 8.12 (d, 1 H, CH, Ph, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (CH_3), 23.2 (CH_2), 28.5 (CH3), 34.3 (CH_2), 40.4 (CH_2), 79.7 (C_q), 119.3 (CH), 120.5 (CH), 120.7 (CH), 124.6 (CH), 125.1 (CH), 125.3 (CH), 127.7 (C_q), 131.1 (C_q), 131.7 (C_q), 132.6 (C_q), 134.7 (C_q), 135.7 (C_q), 136.0 (C_q), 136.3 (C_q), 136.4 (C_q), 136.5 (C_q), 138.3 (C_q), 139.9 (C_q), 140.1 (C_q), 156.1 (C_q), 162.6 (C_q). MS (EI$^+$): *m/z* (%) = 413 (85), 514 (70), 529 (40), 552 (65), 572 (100), 672 (95) $[M]^+$. HRMS-EI$^+$: *m/z* $[M]^+$ calculated for $C_{36}H_{36}N_2O_3S_4$: 672.160881; found: 672.163510. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 403 (4.09), 363 (4.06), 246 nm (4.67).

_N_-(2-Boc-aminoethyl)tetrathia[7]helicene-2'-yl-1-carboxy amide 15

To a flask containing 2-tetrathiahelicenecarboxylic acid **13** (0.041 g, 0.092 mmol), $SOCl_2$ (1 mL, 13.7 mmol) was added under a nitrogen atmosphere. The solution was stirred 1 h at 50 °C then was evaporated under vacuum. The residue was diluted with dry toluene (1 mL) then evaporated. To a solution of the acyl chloride in dry THF (1 mL), a solution of *N*-Boc-ethylenediamine (0.029 g, 0.18 mmol) in DIPEA (50 μL, 0.29 mmol) and dry THF (2 mL) was added. The solution was stirred at 50 °C for 2 h then diluted with CH_2Cl_2 (5 mL) and washed with a saturated solution of NaCl (7 mL). After separation, the aqueous phase

was extracted with CH_2Cl_2 (2 × 10 mL) then the collected organic phases were dried over Na_2SO_4, filtered and evaporated under vacuum. The product was purified by flash chromatography on silica gel (hexane-AcOEt = 7:3) to give compound **15** as yellow solid in 75% yield (40 mg). Mp 172-178 °C. IR (Nujol, cm^{-1}): 3307, 1688, 1632, 1531, 1276, 1172. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, $C(CH_3)_3$), 3.20 - 3.30 (m, 3 H, CH_2), 3.35 - 3.45 (m, 1 H, CH_2), 4.85 (bs, 1 H, NH), 5.35 (bs, 1 H, NH), 6.65 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 6.91 (s, 1 H, CH, thiophene), 6.95 (d, 1 H, CH, thiophene, *J* = 5.5 Hz), 7.93 (d, 1 H, CH, Ph, *J* = 8.5 Hz), 7.98-8.02 (m, 4 H, CH, Ph), 8.14 (d, 1 H, CH, Ph, *J* = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4 (CH_3), 40.3 (CH_2), 40.5 (CH_2), 79.7 (C_q), 119.3 (CH), 120.6 (CH), 120.7 (CH), 121.0 (CH), 121.2 (CH), 124.9 (CH), 125.1 (CH), 125.3 (CH), 129.5 (C_q), 130.4 (C_q), 131.0 (C_q), 134.9 (C_q), 135.9 (C_q), 136.1 (C_q), 136.5 (C_q), 137.1 (C_q), 137.3 (C_q), 137.7 (C_q), 137.9 (C_q), 138.3 (C_q), 157.0 (C_q), 162.5 (C_q). MS (EI^+): *m/z* (%) = 368 (85), 401 (45), 430 (100), 445 (60), 470 (30), 488 (35), 588 (55) $[M]^+$. HRMS-EI^+: *m/z* calculated for $C_{30}H_{24}N_2O_3S_4$: 588.066980; found: 588.067500 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246.0 (4.7), 292.0 (4.3), 324.0 (4.3), 382.0 (4.2), 401.5 nm (4.3).

Synthesis of 2,13-Diiodo-7,8-di-*n*-propyltetrathia[7]helicene 17

To a solution of helicene **16** (309 mg; 0,64 mmol; 1 eq) in dry THF (38 mL), *n*-BuLi (C = 1,5 M in hexane; 1.06 mL, 2,5 eq) was dropped at –78 °C under a nitrogen atmosphere. After 1 h at –78 °C, a solution of I_2 (522 mg; 2,0 mmol; 3,2 eq) in dry THF (2 mL) was dropped, then the mixture was stirred at –78 °C for 1.5 h. The course of the reaction was monitored by TLC (eluent: hexane). The reaction was quenched at –78 °C with a saturated solution of Na_2SO_3, and warm to rt. The yellow suspension was filtered to yield pure product **17** (470 mg, 0.64 mmol, quantitative yield) as light-yellow solid. R_f = 0,33 (hexane); mp 233-235 °C . IR (Nujol, cm^{-1}): 1322, 1155. ^1H-NMR ($CDCl_3$, 300 MHz): δ 1.15 (t, 6 H, CH_3, *J* = 7.3 Hz), 1.75-1.95 (m, 4 H, CH_2), 3.03-3.20 (m, 4 H, CH_2─Ph), 6.93 (s, 2 H, CH, thiophene), 7.90 (d, 2 H, CH, Ph, *J* = 8.5 Hz), 7.93 (d, 2 H, CH, Ph, *J* = 8.5 Hz). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 14.8 (CH_3), 23.7 (CH_2), 34.7 (CH_2), 76.1 (C_q–I), 119.2 (CH), 119.9 (CH), 128.0 (C_q), 130.0 (C_q), 133.1 (C_q), 135.8 (CH), 136.7 (C_q), 136.8 (C_q), 140.3 (C_q), 142.0 (C_q). MS (EI^+): *m/z* (%) 738 $[M]^+$ (100), 709 (10), 582 (15), 440 (7). HMRS (EI^+): *m/z* calculated for $C_{28}H_{20}S_4I_2$: 737.853742, found: 737.857730 $[M]^+$. UV-Vis (CH_2Cl_2): λ_{max} (log ε): 400.0 (4.40), 381 (4.34), 320 (4.40), 287 (4.56), 245 nm (4.71).

Synthesis of 7,8-di-*n*-Pr-2,13-dihydroxycarbonylvinyltetrathia[7]helicene 19

The helicene **5** (65.4 mg, 0.10 mmol) was dissolved in MeOH (5 mL), H_2O (5 mL) and aqueous NaOH (32%; 10.8M; 15 mL). The mixture was refluxed for 3 h then, at rt, an aqueous solution of HCl 10% was added until pH = 1 and the mixture was diluted with CH_2Cl_2 (15 mL). The phases were separated, the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL), then the collected organic phases were dried over

Na_2SO_4 and the solvent was evaporated under vacuum. The product **19** (60 mg, 95% yield) was isolated as yellow solid. R_f = 0.3 (MeOH/AcOEt = 1:1); mp 316-320 °C. IR (Nujol, cm^{-1}): 1716-1682, 1615. ^{1}H-NMR (300 MHz, DMSO-*d*$_6$): δ = 1.11 (t, 6 H, CH_3, *J* = 7.3 Hz), 1.84-1.79 (m, 4 H, CH_2), 3.28-3.00 (m, 4 H, CH_2-Ph), 5.89 (d, 2 H, CH=, *J* = 15.6 Hz), 6.82 (s, 2 H, CH, thiophene), 7.10 (d, 2 H, CH=, *J* = 15.6 Hz), 8.23 (d, 2 H, CH, Ph, *J* = 8.6 Hz), 8.28 (d, 2 H, CH, Ph, *J* = 8.6 Hz), 12.4 (bs, 1 H). ^{13}C-NMR (75 MHz, DMSO-*d6*): δ = 14.4 (CH_3), 22.8 (CH_2), 33.7 (CH_2), 119.6 (CH), 121.0 (CH), 121.4 (CH), 127.0 (C_q), 128.7 (CH), 130.3 (C_q), 132.3 (C_q), 134.7 (C_q), 136.0 (C_q), 136.3 (CH), 136.9 (C_q), 137.2 (C_q), 139.4 (C_q), 166.6 (C_q). MS (EI^+): *m/z* (%) 626 $[M]^+$ (90), 582 (100). HRMS (ESI^+): *m/z* calculated for $C_{34}H_{26}O_4S_4$: 626,071397 found: 626.072510 $[M]^+$. UV-Vis (CH_2Cl_2): λ_{max} (log ε): 427.0 (4.21), 371.0 (4.37), 318.0 (4.45), 260 (4.50), 231.5 nm (4.45).

Synthesis of 1,2-Bis(ethoxycarbonyl)-1,2-bis(benzodithien-2'-yl)ethene 20

To a solution of tris(dimethylamino)phosphine (174 μL, 0.96 mmol) in dry CH_2Cl_2 (1 mL), a solution of **22** (553 mg, 1.91 mmol) in dry CH_2Cl_2 (3 mL) was added at –70 °C under a N_2 atmosphere. After 10 min sulfur powder (7 mg, 0.21 mmol) was added, the mixture was stirred for 30 min at –70 °C and then 2 h at rt. The brown solution was quenched with H_2O (20 mL), and diluted with CH_2Cl_2 (15 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: with a gradient from hexane to AcOEt) to yield the product **20** as orange solid (418 mg, 80% yield, 75/25 mixture of two isomers) and starting material **22** (99 mg, 18% yield). From the chromatography we were able to isolate a fraction containing the major diastereoisomer. IR (Nujol, cm^{-1}) = 1719, 1701. MS (ESI^+): *m/z* = 571 $[M + Na]^+$, 1119 $[2M + Na]^+$. HRMS (ESI^+): *m/z* calculated for $C_{28}H_{20}S_4O_4Na$: 571.01366, found: 571.01266 $[M]^+$; calculated for $C_{56}H_{40}S_8O_8Na$: 1119.03810 found: 1119.03530 $[M+Na]^+$. *Anal.* Calcd for $C_{28}H_{20}S_4O_4$: C, 61.29; H, 3.67. Found: C, 61.56; H, 4.08. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 370.5 (3.35), 294 (4.22), 237 nm (4.60). Mp 205-7 °C. Major diastereoisomer ^{1}H (200 MHz, DMSO-*d*$_6$) δ = 1.28 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.35 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.84 (d, 2 H, CH, Ph, *J* = 8.7 Hz), 7.91 (d, 2 H, CH, thiophene, *J* = 5.5 Hz), 8.02-7.98 (m, 2 H), 8.14 (s, 2 H, CH, thiophene). ^{13}C (75 MHz, DMSO-*d*$_6$) δ = 13.8 (CH_3), 62.0 (CH_2), 118.5 (CH), 120.8 (CH), 122.6 (CH), 127.5 (CH), 128.5 (CH), 132.1 (C_q), 133.5 (C_q), 134.7 (C_q), 135.1 (C_q), 136.3 (C_q), 138.4 (C_q), 165.7 (C_q). ^{1}H (200 MHz, $CDCl_3$,) δ = 1.36 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.42 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.57 (d, 2 H, CH, thiophene, *J* = 5.5 Hz), 7.63 (d, 2 H, CH, Ph, *J* = 8.7 Hz), 7.65 (d, 2 H, CH, thiophene, *J* = 5.5 Hz), 7.80 (d, 2 H, CH, Ph, *J* = 8.7 Hz), 7.81 (s, 2 H, CH, thiophene). ^{13}C (75 MHz, $CDCl_3$) δ = 14.04 (CH_3), 62.2 (CH_2), 118.4 (CH), 120.2 (CH), 121.9 (CH), 126.6 (CH), 127.1 (CH), 132.6 (C_q), 133.8 (C_q), 134.9 (C_q), 135.8 (C_q), 136.6 (C_q), 139.2 (C_q), 166.5 (C_q). Mixture of two isomers:

^{1}H (300 MHz, $CDCl_3$) δ = 1.14 (t, 6 H, CH_3, *J* = 7.1 Hz) 1.36 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.26 (q, 4 H, CH_2, *J* = 7.1 Hz), 4.40 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.55 (d, 2 H, CH, thiophene, *J* = 5.4 Hz), 7.58-7.64 (m, 6 H), 7.68 (d, 2 H, CH, thiophene, *J* = 5.4 Hz), 7.75 (d, 2 H, CH, Ph, *J* = 8.7 Hz,), 7.77-7.80 (m, 4 H), 7.83-7.86 (m, 4 H).^{13}C (75 MHz, DMSO-d_6) δ = 13.5 (CH_3), 13.8 (CH_3), 62.0 (CH_2), 62.4 (CH_2), 118.3 (CH), 118.4 (CH), 120.7 (CH), 122.5 (CH), 122.6 (CH), 124.5 (CH), 127.4 (CH), 128.4 (CH), 128.5 (CH), 133.5 (C_q), 133.6 (C_q), 134.5 (C_q), 134.7 (C_q), 135.0 (C_q), 135.2 (C_q), 136.2 (C_q), 136.5 (C_q), 136.9 (C_q), 138.3 (C_q), 166.5 (C_q).

Synthesis of 1,2-Bis(ethoxycarbonyl)-1,2-bis(benzodithien-2'-yl)ethene 20 from McMurry coupling

To a solution of **22** (196.7 mg, 0.678 mmol) in dry THF (6 mL), $TiCl_4$ (268 mg, 1.4 mmol, 155 μL, d = 1.73 g/mL) was added dropwise at 0 °C under a nitrogen atmosphere. After 2 min, solid Zn (61.4 mg, 0.939 mmol) was added and the mixture was stirred at rt for 5 min then refluxed for 4 h. The mixture was cooled at rt, quenched with cooled water (0-2 °C, 20 mL), then diluted with a saturated solution of NaCl (10 mL) and CH_2Cl_2 (40 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 35 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: gradient from light petroleum/AcOEt 8:2 to AcOEt, then MeOH/AcOEt = 1:1) isolating only one isomer of the product **20** (48 mg, 13% yield, mp 205-7 °C) and the product **25** (26 mg, 14% yield) as yellow solid.

2-Benzodithien-2'-yl ethyl acetate 25

R_f = 0,3 (hexane/AcOEt 9:1); mp 95-97 °C. IR (Nujol, cm^{-1}) = 1732. ^{1}H (200 MHz, $CDCl_3$) δ = 1.30 (t, 3 H, CH_3, *J* = 7.1 Hz), 3.98 (s, 2 H, CH_2), 4.22 (q, 2 H, CH_2, *J* = 7.1 Hz), 7.53 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.56 (s, 1 H, CH, thiophene), 7.65 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.72 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 7.78 (d, 1 H, CH, Ph, *J* = 8.7 Hz). ^{13}C (75 MHz, $CDCl_3$) δ = 14.2 (CH_3), 36.5 (CH_2), 61.4 (OCH_2), 118.4 (CH), 118.6 (CH), 121.6 (CH), 121.8 (CH), 126.4 (CH), 134.3 (C_q), 134.6 (C_q), 136.5 (C_q), 170.0 (CO). MS (EI^+): *m/z* (%) = 276 (45) $[M]^+$, 203 (100). HRMS (EI^+): *m/z* calculated for $C_{14}H_{12}O_2S_2$: 276.027873, found: 276.027620 $[M]^+$.

Synthesis of 2-(Benzodithien-2'-yl)- 2- oxoethyl acetate 22

To a solution of benzodithiophene **23** (1 g, 5,3 mmol) in dry THF (30 mL), *n*-BuLi (1.6 M, 3.6 mL, 5,79 mmol) was dropped at –78 °C under a nitrogen atmosphere. The resulting yellow solution was stirred at –78 °C for 1 h forming a yellow suspension that was dropped, in 45min under a nitrogen atmosphere and at –78 °C, into a second dried flask containing diethyl oxalate (2.5 mL, 18.44 mmol) in dry THF (7 mL) at rt The final solution was stirred for 30 min at rt. The reaction was quenched with a saturated solution of

NH_4Cl (100 mL), and extracted with CH_2Cl_2 (1×400 mL and 2 × 200 mL) and with AcOEt (1 × 300 mL). The organic phases were dried over Na_2SO_4, filtered over celite and evaporated under vacuum. The residue was purified by flash chromatography on silica gel (eluent: with a gradient from hexane to AcOEt) to yield pure product **22** (1 g, 65% yield) as yellow-orange solid, the by-product **24** (207 mg, 10% yield) as orange solid and recovering 5% of the starting material **23** with unidentified by-products.

2-(Benzodithien-2'-yl)- 2- oxoethyl acetate 22

R_f = 0.5 (hexane/AcOEt = 9:1); mp 87-88 °C. IR (Nujol, cm^{-1}) = 1729, 1654, 1140-1165. ^1H (200 MHz, $CDCl_3$): δ = 1.48 (t, 3 H, CH_3, *J* = 7.1 Hz), 4.50 (q, 2 H, CH_2, *J* = 7.1 Hz), 7.68 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.79 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.82 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 7.99 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 8.79 (s, 1 H CH, thiophene). ^{13}C (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 62.6 (CH_2), 118.1 (CH), 121.5 (CH), 122.9 (CH), 128.0 (CH), 131.9 (CH), 133.5 (C_q), 135.8 (C_q), 136.7 (C_q), 138.0 (C_q), 141.5 (C_q), 161.1 (C_q), 177.1 (C_q). MS (EI^+): *m/z* (%) = 290 $[M]^+$ (20), 217 (100). HRMS (EI^+): *m/z* calculated for $C_{14}H_{10}S_2O_3$: 290.007138 found: 290.003170 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 369 (4.30), 271 (3.98), 232.5 nm (4.46).

2,2'-(Benzodithien- 2',7'-di-yl)- di-(2,2'-oxoethyl acetate) 24

R_f = 0.3 (hexane/AcOEt = 9:1); mp 144-146 °C. IR (Nujol, cm^{-1}) = 1724, 1665, 1296,1189-1138. ^1H (300 MHz, $CDCl_3$): δ = 1.51 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.57 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.95 (s, 2 H), 8.77 (s, 2 H). ^{13}C (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 63.1 (CH_2), 123.0 (CH), 131.6 (CH), 135.4 (C_q), 139.8 (C_q), 142.5 (C_q), 161.2 (C_q), 177.3 (C_q). MS ($ESI)^+$: *m/z* = 413 $[M+Na]^+$, 803 $[2M+Na]^+$. HRMS (ESI^+): *m/z* calculated for $C_{18}H_{14}S_2O_6Na$: 413.01240 found: 413.01221 $[M+Na]^+$; calculated for $C_{36}H_{28}S_4O_{12}Na$: 803.03558 found: 803.03682 $[2M+Na]^+$.

Synthesis of (*E,Z*)-Ethyl 3-hydroxy-2,4-bis(benzodithien-2',2''-di-yl)but-2-enoate 26 and 2-(benzodithien-2'-yl)-2-hydroxyethyl acetate 27

$TiCl_4$ (270 μl, 2.47 mmol) was added dropwise to dry THF (20 mL) cooled at 0 °C under a nitrogen atmosphere. After 2 min solid Zn (467 mg, 5.08 mmol) was added and the mixture was stirred at rt for 5 min then refluxed for 2 h. The mixture was cooled to 40 °C then pyridine (191 μL, 2.47 mmol) was added. The mixture was refluxed for 30 min, cooled to rt, and a solution of **22** (476 mg, 1.64 mmol) in dry THF (10 mL) was added. The red solution was refluxed for 12 h 30 min, cooled to rt, quenched with aqueous HCl (6 N, 20 mL) and diluted with CH_2Cl_2 (20 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: with a gradient from hexane/AcOEt = 8:2 to AcOEt) to yield product **26** as white solid (71 mg, 17% yield) as single isomer, product **27** as orange oil (134 mg, 28%

yield) and **25** as yellow solid (36 mg, 8% yield).

(*Z*)-Ethyl 3-hydroxy-2,4-bis(benzodithien-2',2''-di-yl) but-2-enoate 26

Mp 146-149 °C. IR (Nujol, cm^{-1}) = 1637, 1605. ^1H (300 MHz, $CDCl_3$) δ = 1.21 (t, 3 H, CH_3, *J* = 7.1 Hz), 3.95 (s, 2 H, CH_2-4), 4.24 (q, 2 H, OCH_2, *J* = 7.1 Hz), 7.41 (s, 1 H, CH-3'', thiophene), 7.49 (s, 1 H, CH-3', thiophene), 7.51 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.53 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.55 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.59 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.71 (d, 1 H, CH, Ph, *J* = 8.6 Hz), 7.72 - 7.78 (m, 2 H, CH, Ph), 7.83 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 13.53 (s, 1 H, OH). ^{13}C (75 MHz, $CDCl_3$) δ = 14.1 (CH_3), 34.8 (CH_2-4), 61.5 (OCH_2), 98 (C_q-2), 118.4 (CH), 118.5 (CH), 118.9 (CH), 121.5 (CH-3''), 121.9 (CH), 124.5 (CH-3'), 126.3 (CH), 126.7 (CH), 134.0 - 134.6 (C_q), 136.3 -136.5 (C_q), 137.8 (C_q), 139.0 (C_q-2''), 172.2 (C_q-1), 175.0 (C_q-3). MS ($APCI^-$): *m/z* = 505 $[M - 1]^-$. HRMS (EI^+): *m/z* calculated for $C_{26}H_{18}O_3S_4Na$: 529.00310, found: 529.00247 $[M+Na]^+$. *Anal.* Calcd for $C_{26}H_{18}O_3S_4$: C, 61.63; H, 3.58. Found: C, 62.39; H, 4.31.

HMBC-NMR experiment showed strong correlations between H-4 with C-3'', C-2'', C-3, C-2; OH with C-2, C-3, C-4; H-3'' with C-4, C-2''; H-3' with C-2, C-2'; $OC\underline{H}_2$ with C-1, $\underline{C}H_3$; and $C\underline{H}_3$ with $O\underline{C}H_2$ confirming the hypothesis of the structure.

NOESY and ROESY-NMR experiments showed strong correlations between OCH_2 and CH_3; H-4 and H-3', H-3'', OH; OH and OCH_2; which would indicate that the compound **26** exists as the Z isomer.

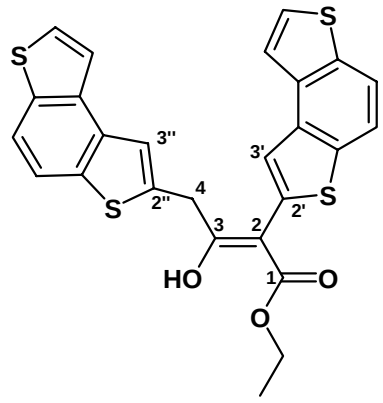


Figure 3. Numbering of compound **26**

2-(Benzodithien-2'-yl)-2-hydroxyethyl acetate 27

R_f = 0,1 (hexane/AcOEt = 9:1). ^1H (300 MHz, $CDCl_3$) δ = 1.33 (t, 3 H, CH_3, *J* = 7.1 Hz,), 3.75 (bs, 1 H, OH), 4.26-4.37 (m, 2 H, CH_2), 5.54 (s, 1 H, CH), 7.54 (d, 1 H, *J* = 5.4 Hz), 7.65 (d, 1 H, *J* = 5.4 Hz), 7.71-7.74 (m, 2 H), 7.79 (d, 1 H, *J* = 8.7 Hz). ^{13}C (75 MHz, $CDCl_3$) δ = 14.0 (CH_3), 62.8 (CH_2), 69.7 (CH), 118.3 (CH), 118.5 (CH), 119.0 (CH), 120.1 (CH), 121.7 (CH), 126.6 (CH), 134.2 (C_q), 134.6 (C_q), 136.3 (C_q), 136.6 (C_q), 142.3 (C_q), 172.1 (CO). MS (EI^+): *m/z* (%) 292 (35) $[M^+]$, 219 (100), 190 (35). HRMS (EI^+): *m/z* calculated for $C_{14}H_{12}O_3S_2$: 292.022788, found: 292.022280 $[M]^+$.

Synthesis of 1,2-*N,N,N,N*-Tetraethyl-bisamine-1,2-bis(benzodithien-2'-yl) ethene 28

To a blue solution of Sm (63 mg; 0,411 mmol) and SmI_2 (159 mg; 0,348 mmol) in dry THF (1 mL), a solution of amide **29** (183 mg; 0,632 mmol) in dry THF (2,5 mL) was added at 68 °C under nitrogen atmosphere. The dark yellow solution was refluxed for 2 h 20 min. The course of the reaction was monitored by TLC (eluent: hexane/AcOEt = 8:2) then the solvent was evaporated under vacuum and the residue purified by flash chromatography on silica gel (eluent: hexane/AcOEt = 8:2) to yield the compound **28** (60 mg, 35% yield) as yellow-orange solid and the starting material **29** (78.5 mg, 43% yield). R_f = 0,7 (hexane/AcOEt = 8:2); mp 185-190 °C. IR (Nujol, cm^{-1}) = 1571, 1642. ^1H (300 MHz, $CDCl_3$) δ = 1.08 (t, 12 H, CH_3, J = 7.2 Hz), 3.13 (q, 8 H, CH_2, J = 7.2 Hz), 7.56 (d, 2 H, CH, thiophene, J = 5.5 Hz), 7.69 (d, 2 H, CH, thiophene, J = 5.5 Hz), 7.70 - 7.76 (m, 4 H, CH, Ph), 7.78 (d, 2 H, CH, Ph, J = 8.6 Hz). ^{13}C (75 MHz, $CDCl_3$) δ = 13.2 (CH_3), 47.5 (CH_2), 118.3 (CH), 118.6 (CH), 120.5 (CH), 121.8 (CH), 126.2 (CH), 134.0 (C_q), 136.2 (C_q), 136.7 (C_q), 137.8 (C_q), 142.8 (C_q), 146.0 (C_q). MS (EI^+): *m/z* (%) = 546 (100) $[M]^+$, 517 (20), 473 (20), 403 (15), 216 (45). HRMS (EI^+): *m/z* calculated for $C_{30}H_{30}N_2S_4$: 546.129186, found: 546.127500 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (4.30), 397 (4.32), 375 (4.24), 312 (4.24), 233 nm (4.62).

Synthesis of *N,N*-Diethyl-benzodithien-2'-yl-carboxyamide 29 from benzodithiophene 23

To a solution of benzodithiophene **23** (100 mg; 0,526 mmol) in dry THF (8 mL), *n*-BuLi (1,6 M in hexane; 0,38 mL; 0,605 mmol) was dropped at –78 °C under nitrogen atmosphere. The resulting white-yellow solution was stirred at –78 °C for 30 min then at rt for 20 min. This suspension was dropped, during the period of 5 min, into a second dried flask under nitrogen atmosphere containing *N,N*-diethyl carbamoyl chloride (1 mL; 7,89 mmol) diluted in dry THF (0,5 mL) at –78 °C. The orange solution was stirred at –78 °C for 30 min and monitored by TLC (eluent: hexane/AcOEt = 7:3). The reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and diluted with CH_2Cl_2 (20 mL). The phases were separated, the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and evaporated under vacuum. The residue (orange oil) was purified by flash chromatography on silica gel (eluent: gradient from hexane to hexane/AcOEt = 2:8) to yield product **29** as yellow-green oil (49 mg, 32% yield), product **31** (33 mg, 16% yield) as yellow solid and ketone **30** (9 mg, 4% yield) as yellow solid.

***N,N*-Diethyl-benzodithien-2'-yl carboxy amide 29**

R_f = 0.1 (hexane/AcOEt = 7:3). IR (film, cm^{-1}) = 3097-3071, 2972-2872, 1622. ^1H (300 MHz, $CDCl_3$) δ = 1.28 (t, 6 H, CH_3, J = 7.1 Hz), 3.59 (q, 4 H, CH_2, J = 7.1 Hz), 7.58 (d, 1 H, CH, thiophene, J = 5.4 Hz), 7.67 (d, 1 H, CH, thiophene, J = 5.4 Hz), 7.75 (d, 1 H, CH, Ph, J = 8.7 Hz), 7.85 (d, 1 H, CH, Ph, J = 8.7 Hz), 7.89 (s, 1 H, CH, thiophene). ^{13}C (75 MHz, $CDCl_3$) δ = 13.7 (CH_3), 42.1 (CH_2), 118.3 (CH), 120.2

(CH), 121.6 (CH), 122.7 (CH), 127.1 (CH), 133.7 (C_q), 134.9 (C_q), 136.8 (C_q), 137.0 (C_q), 137.7 (C_q), 164.2 (CO). MS (EI^+): *m/z* (%) = 289 (45) $[M]^+$, 217 (100), 189 (40). HRMS (EI^+): *m/z* calculated for $C_{15}H_{15}NOS_2$: 289.059508, found: 289.059750 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 306.5 (4.31), 229.5 nm (4.54).

Bis(benzodithien-2-yl) ketone 30

R_f = 0.4 (hexane/AcOEt = 7:3); mp = 234-236 °C. IR (Nujol, cm^{-1}) = 1598, 1505. ^1H (300 MHz, $CDCl_3$) δ = 7.67 (d, 2 H, CH, thiophene, *J* = 5.4 Hz), 7.80 (d, 2 H, CH, thiophene, *J* = 5.4 Hz), 7.86 (d, 2 H, CH, Ph, *J* = 8.7 Hz), 7.98 (d, 2 H, CH, Ph, *J* = 8.7 Hz), 8.59 (s, 2 H, CH, thiophene). ^{13}C (75 MHz, $CDCl_3$) δ = 118.7 (CH), 121.9 (CH), 122.3 (CH), 128.0 (CH), 128.4 (CH), 134.1 (C_q), 135.9 (C_q), 137.2 (C_q), 140.2 (C_q), 142.0 (C_q), 181.5 (CO). MS ($APCI^+$): *m/z* = 407 $[M+1]^+$. MS (EI^+): *m/z* (%) = 406 (100) $[M^+]$, 217 (70), 189 (50). HRMS (EI^+): *m/z* calculated for $C_{21}H_{10}OS_4$: 405.961452, found: 405.961910 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 372 (4.33), 330 (4.18), 240 nm (4.52).

***N,N,N,N*-Tetraethylbenzodithiene-2,7-di-ylcarboxyamide 31**

R_f = 0,1 (hexane/AcOEt = 8:2); mp 151-153 °C. IR (Nujol, cm^{-1}) = 1624, 1599, 1507. ^1H (300 MHz, $CDCl_3$) δ = 1.28 (t, 12 H, CH3, *J* = 7.1 Hz), 3.58 (q, 8 H, CH_2, *J* = 7.1 Hz), 7.79 (s, 2 H), 7.86 (s, 2 H). ^{13}C (75 MHz, $CDCl_3$) δ = 13.7 (CH_3), 42.1 (CH_2), 119.8 (CH), 122.5 (CH), 134.1 (C_q), 137.3 (C_q), 138.4 (C_q), 163.9 (CO). MS (EI^+): *m/z* (%) = 388 (60) $[M^+]$, 316 (100), 216 (45); 188 (35). HRMS (EI^+): *m/z* calculated for $C_{20}H_{24}N_2O_2S_2$: 388.127922, found: 388.127560 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 316 nm (4.36).

Synthesis of *N,N*-Diethylbenzodithien-2'-ylcarboxyamide 29 from the benzodithiophenecarboxylic acid 34

Under a nitrogen atmosphere, a suspension of **34** (390 mg; 1,665 mmol) in $SOCl_2$ (13 mL) was heated at 65 °C for 2 h obtaining a clear solution. The $SOCl_2$ was evaporated, the residue was dissolved in dry THF (18 mL) at rt and *N,N*-diethylamine (2 mL; 19,41 mmol) was added. The yellow suspension was stirred at rt for 1 h and 45 min. The course of reaction was monitored by TLC (eluent: hexane/AcOEt = 8:2), then the mixture was quenched by a saturated aqueous solution of $NaHCO_3$ (30 mL) and diluted with CH_2Cl_2 (40 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: hexane/AcOEt = 8:2) obtaining the amide **29** as yellow-green oil (476 mg, 99% yield).

Synthesis of 2-Ethoxycarbonylbenzodithiophene 32

To a solution of benzodithiophene **23** (1 g, 5,26 mmol) in dry THF (70 mL), *n*-BuLi (1,47 M in hexane;

3,7 mL; 5,53 mmol) was dropped at –78 °C under a nitrogen atmosphere. The resulting yellow suspension was stirred at –78 °C for 1 h then at rt for 15 min. At –78 °C $ClCO_2Et$ (1,5 mL; 1,71 g; 15,79 mmol) was added and the mixture was stirred 5 min at –78 °C then 15 min at rt. The course of reaction was monitored by TLC (eluent: hexane/AcOEt = 9:1) then the reaction was quenched with a saturated aqueous solution of NH_4Cl (40 mL) and diluted with CH_2Cl_2 (130 mL). The phases were separated, the aqueous phase was extracted with CH_2Cl_2 (1 × 50 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The residue (orange solid) was purified by column chromatography on silica gel (eluent: gradient from hexane to AcOEt) to yield product **32** as pale yellow solid (1 g, 74% yield), the by-product **33** as yellow solid (246 mg, 14% yield) and the starting material **23** as white solid (20 mg, 2% yield).

2-Ethoxycarbonylbenzodithiophene 32

R_f = 0.5 (hexane/AcOEt = 9:1); mp 97-99 °C. IR (Nujol, cm^{-1}) = 1714, 1514. ^1H (200 MHz, $CDCl_3$) δ = 1.45 (t, 3 H, CH_3, *J* = 7.1 Hz), 4.44 (q, 2 H, CH_2, *J* = 7.1 Hz), 7.63 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.73 – 7.80 (m, 2 H), 7.93 (d, 1 H, CH, Ph, *J* = 8.8 Hz), 8.42 (s, 1 H, CH, thiophene). ^{13}C (300 MHz, $CDCl_3$) δ = 14.4 (CH_3), 61.6 (CH_2), 118.7 (CH), 121.6 (CH), 121.9 (CH), 127.6 (CH), 128.1 (CH), 133.7 (C_q), 133.8 (C_q), 135.6 (C_q), 136.9 (C_q), 139.6 (C_q), 162.8 (CO). MS (EI^+): *m/z* (%) = 262 (100) $[M]^+$, 234 (65), 217 (60), 189 (35). HRMS (EI^+): *m/z* calculated for $C_{13}H_{10}O_2S_2$: 262.012223, found: 262.012510 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 318 (4.18), 272 (3.77), 229.5 nm (4.27).

2,7-Bis(ethoxycarbonyl)-benzodithiophene 33

R_f = 0,3 (hexane/AcOEt = 9:1); mp 153-156 °C. IR (Nujol, cm^{-1}) = 1720, 1244. ^1H (200 MHz, $CDCl_3$) δ = 1.44 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.43 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.80 (s, 2 H), 8.32 (s, 2 H). ^{13}C (75 MHz, $CDCl_3$) δ = 14.3 (CH_3), 61.7 (CH_2), 121.3 (CH), 127.6 (CH), 134.6 (C_q), 134.7 (C_q), 139.8 (C_q), 162.5 (CO). MS (EI^+): *m/z* (%) = 334 (100) $[M^+]$, 306 (20), 289 (40), 278 (30), 261 (45), 233 (25), 189 (35). HRMS (EI^+): *m/z* calculated for $C_{16}H_{14}O_4S_2$: 334.033353, found: 334.032560 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 344 (4.59), 327 (4.65), 231 nm (4.72).

Synthesis of Benzodithien-2-yl-carboxylic acid 34

A white suspension of ester **32** (506 mg; 1,908 mmol) in EtOH (30 mL), H_2O (15 mL) and aqueous NaOH (32%; 10,8 M; 25 mL) was heated at 50 °C for 45 min. The course of reaction was monitored by TLC (eluent: hexane/AcOEt = 9:1), the colourless solution was cooled at 0 °C then an aqueous solution of HCl (18%, 30 mL) was added until pH = 1. The solution was diluted with CH_2Cl_2 (100 mL), the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (1 × 50 mL). The collected organic phases were dried over Na_2SO_4, filtered over celite and the solvent was evaporated under vacuum. The yellow-white residue was dissolved in CH_2Cl_2 (10 mL) and precipitated by pentane (30 mL). The

suspension was filtered to yield white product **34** (446 mg, quantitative yield). R_f = 0,2 (AcOEt); mp 259-261 °C. IR (Nujol, cm^{-1}) = 1674.9, 1512.9. ^1H (200 MHz, DMSO-d_6) δ = 7.97 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 7.99 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 8.12 (d, 1 H, CH, thiophene, *J* = 5.4 Hz), 8.14 (d, 1 H, CH, Ph, *J* = 8.7 Hz), 8.65 (s, 1 H, CH, thiophene), 11.15 (bs, 1 H).^{13}C (75 MHz, DMSO-d_6) δ = 118.8 (CH), 121.8 (CH), 122.7 (CH), 128.5 (CH), 128.7 (CH), 133.7 (C_q), 134.6 (C_q), 135.5 (C_q), 136.4 (C_q), 138.7 (C_q), 163.4 (CO). MS (EI^+): *m/z* (%) = 234 (100) [M^+], 217 (30), 189 (20). HRMS (EI^+): *m/z* calculated for $C_{11}H_6O_2S_2$: 233.980923, found: 233.980710 $[M]^+$. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 321.5 (4.15), 272 (3.75), 229.5 nm (4.25).

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