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Synthesis of [1,3]Dithiole and Spiro[1,3]dithiole Thiopyran Derivatives of the [1,2]Dithiolo[1,4]thiazine Ring System

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Received January 7, 2002

We report the synthesis of some new polysulfur−nitrogen heterocycles by cycloaddition reactions to readily available tricyclic condensed 1,2-dithiole-3-thiones. Thus, treatment of bis[1,2]-dithiolopyrrole ketothione **1** with diacyl acetylenes gave the bis-aducts **2a**−**d**. On the other hand, cycloaddition of bis[1,2]dithiolo[1,4]thiazine ketothione **3** with 1 equiv of acyl or diacyl acetylenes gave [1,3]dithiolylidenyl[1,2]dithiolo[1,4]thiazines **4a**−**f** in fair to high yields. Catalysis by scandium triflate was used in the reactions that implied the less reactive dipolarophiles. Treatment of **3** with 2 equiv of DBA gave the bis-aduct **5a**, and reaction of **4c** with DMAD gave the mixed bis-adduct **5b**. Cyclic voltammetry of selected examples showed irreversible processes that were influenced by the electrochemical activity of peripheral groups bonded to the heterocyclic system.

Introduction

The concept of aromaticity is a powerful tool in heterocyclic chemistry for the de novo prediction and preparation of new heterocyclic systems,[1] as well as for the understanding of transition states for heterocycloaddition reactions.[2] Searching for new stable heterocycles that fit the rules of aromaticity, we have prepared some new aromatic pseudoazulenes[3] and many pseudoaromatic bis[1,2]dithiolo[1,4]thiazines,[4] bis[1,2]dithiolopyrroles,[5] a [1,2]dithiolo[1,4]thiazine,[6] bis[1,2]dithiolylamines,[7] and 1,2-dithiolodisulfides[8] all in one-pot multicomponent reactions. We are now studying the exceptional reactivity of some of these heterocycles. As classic 1,3-dipolar reagents,[9] the already prepared monocyclic 1,2-dithiol-3-thiones reacted with dimethyl acetylenedicarboxylate (DMAD), giving sulfur-rich 1:1 adducts,[8] but the reaction of polycyclic bisdithiolopyrroles and DMAD initially gave instead complex poly-adducts.[5a] There are very few reported examples of multiple additions of DMAD to polycyclic bis-1,2-dithiol-3-thiones,[10] and the reported results do not permit a good prediction of reactivity for new heterocyclic systems, so we decided to investigate the unexpected behavior of fused dithiolethiones in cycloaddition reactions with dipolarophiles, as a fast way to new polycyclic heterocycles. In this paper we report the reactions of the bisdithiolopyrrole **1** and the bis-dithiolothiazine **3** with bis-substituted acetylenes and a structural study of the experimental results.

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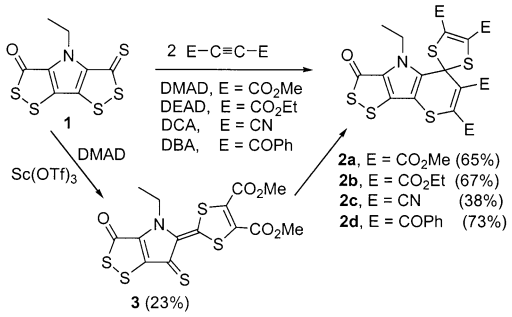
10.1021/jo020015a CCC: $22.00
Published on Web 08/07/2002

SCHEME 1



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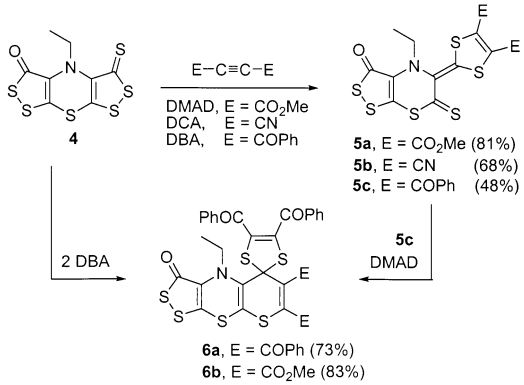

Results and Discussion

We first subjected the bis[1,2]dithiolopyrrole **1**, obtained in one-pot reaction from commercial *N*-ethyldiisopropylamine and disulfur dichloride (S_2Cl_2),[4b] to reaction with typical dipolarophiles. Thus, the reaction of **1** (1 equiv) and DMAD (2.5 equiv) in refluxing toluene for 2 h gave product **2a**, as a yellow solid (mp 218−220 °C, 65%) after chromatography (Scheme 1). Mass spectrometry, HRMS, and microanalysis showed **2a** to be a 1:2 adduct with $C_{20}H_{17}NO_9S_5$. Its ^{13}C NMR showed four carbonyl groups, six sp^2-tertiary carbon signals, one sp^3-quaternary carbon, one methylene, and five methyl groups. Its ^1H NMR showed one methylene and five methyl groups, all consistent with the spiro[1,3]dithiolothiopirane structure **2a**. Analogously, the reaction of **1** (1 equiv) and diethyl acetylenedicarboxylate (DEAD) (2.5 equiv) and dicyanoacetylene[11] (DCA) (2.5 equiv) or dibenzoylacetylene[12] (DBA) (2.5 equiv) in refluxing toluene (DEAD) or benzene (DCA or DBA) for 0.5−2 h gave, respectively, products **2b**−**d**, as yellow solids (38−73%) characterized by spectroscopy and microanalysis. The differences in the reactivity of **1** and the activated acetylenes were evidenced by the differences in the requisite temperature and time of every reaction, showing that DBA was more reactive than DCA and this one more reactive than DMAD or DEAD, but there was no difference in the structure of the obtained products that were in all cases the 1:2 adducts. By monitoring every reaction by TLC we noticed that, at the beginning of every reaction under reflux, a green spot appeared which thereafter disappeared as starting materials were disappearing and converted to the corresponding product **2a**−**d**, which was seen on the TLC plate as the only recognizable product at the end of every reaction. We concluded that under thermal conditions the first cycloaddition reaction of **1** and DMAD, DEAD, DCA, or DBA was more energetically demanding than the corresponding reaction of the expected highly reactive 1:1 cycloadduct and the same acetylenes; therefore, the 1:2 cycloadduct was the only product obtained in all thermal cycloadditions. In search for the intermediate 1:1 adduct, we performed the reaction of **1** (1 equiv) and DMAD (1 equiv) in the presence of scandium triflate [$Sc(OTf)_3$] (50% mol), a typical catalyst for cycloadditions,[13] in refluxing dichloromethane for 2 h. Quick preparative TLC of the reaction residue afforded product **3**, as a green solid [mp 117 °C (dec), 23%] (Scheme 1). Its ^1H NMR showed a methylene, two very close methoxy, and one methyl group, and HRMS gave an elemental composition of the molecular ion peak of $C_{14}H_{11}NO_5S_5$, all consistent with the structure of a 1:1 adduct. Product **3** reacted with 1 equiv of DMAD in refluxing toluene for a few minutes, to give **2a** in quantitative yield. It showed a maximum UV absorption at 616 nm and was highly photosensitive, decomposing after a few minutes under sunlight irradiation in a dichloromethane solution. On standing, product **3** slowly decomposed to starting material **1** and baseline on TLC. MS showed a peak at 291 uma with a relative abundance of 76%, confirming the easy loss of DMAD. Attempts to increase the yield of **3** by increasing reaction temperature always conducted to the thermal second cycloaddition, thus giving the 1:2 adduct **2a**. The reaction of **1** and other dipolarophiles (DBA, di-*tert*-butyl acetylenedicarboxylate) in the same conditions afforded unstable green compounds that decomposed during workup.

Monocyclic and some bicyclic 1,2-dithiole-3-thiones cycloadd to one[9,14] or two[9,10,15] molecules of activated acetylenes bearing one or two electron-acceptor groups, depending on the reactivity of the dithiolethione and the dipolar reagent, but there is not a clear rule for prediction. To compare with the latter results, we studied the reactivity of the bis[1,2]dithiolo[1,4]thiazine **4**, easily obtained in one-pot reaction from commercial *N*-ethyldiisopropylamine and S_2Cl_2,[4b] and the same dipolarophiles. As in previous cases, the reaction of **4** (1 equiv) and DMAD (2.5 equiv) in refluxing benzene was monitored by TLC. In 10 min the starting material had disappeared, giving product **5a**, as a red solid (mp 159−160 °C, 81%) after chromatography (Scheme 2). Mass spectrometry, HRMS, and microanalysis showed that the product corresponded to a 1:1 adduct with the molecular formula $C_{14}H_{11}NO_5S_6$. Its ^{13}C NMR spectrum showed a thiocarbonyl group (δ 192) and three carbonyl groups (δ 185, 161, and 160) (confirmed by IR spectroscopy), six sp^2-tertiary carbon signals, and two alkyl signals. Its ^1H NMR spectrum showed three methyl groups and two

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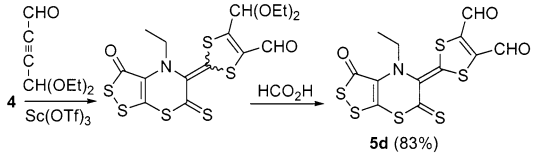
diastereotopic methylenic protons (two sextets), indicating the unexpected presence of conformers. Thus the structure of dimethyl 3-oxo-4-ethyl-5-(1,3-dithiol-2-ylidenyl)-6-thioxo[1,2]dithiolo[3,4-*b*][1,4]thiazine-4′,5′-dicarboxylate **5a** was assigned. Under similar conditions, **4** (1 equiv) reacted with DCA (2.5 equiv) in refluxing benzene for 10 min, to give the 1:1 adduct **5b**, as a red solid (mp 173−175 °C, 68%), fully characterized by spectroscopic and analytical data. The reaction of **4** (1 equiv) and DBA (1 equiv) in refluxing benzene for 5 min also gave the 1:1 adduct **5c**, a red solid of mp 78−79 °C, but in much lower yield (48%). In addition, the reaction of **4** (1 equiv) with excess DBA (2.5 equiv) in refluxing benzene for 30 min gave a new product **6a**, as a yellow solid (mp 104−106 °C, 73%). Mass spectrometry (FAB) of **6a** showed a molecular peak of 792 amu, corresponding to the protonated 1:2 adduct of **4** plus two molecules of DBA. The molecular formula of **6a** was confirmed by microanalysis. Its ^{13}C NMR spectrum did not show any thiocarbonyl group but showed five carbonyl groups (δ 193, 190, 188, 186, and 183) (confirmed by IR spectroscopy), 24 unsaturated carbon signals, one sp^3 quaternary carbon (δ 71) and two alkyl signals. Its ^{1}H NMR spectrum showed 20 aromatic protons, one methyl group, and two diastereotopic methylenic protons (two groups of six signals), indicating again the presence of conformers. In consequence, the structure of spiro[1,3]dithiolothiopyrane **6a** was assigned (Scheme 2). Compound **6a** was easily obtained from **4** and DBA; in fact, a small excess of DBA in the reaction mixture was sufficient for the formation of traces of **6a** in refluxing benzene. In consequence, the yield of **5c** was lower than expected and the separation of mixtures complicated the reaction workup. We therefore looked for milder conditions for the preparation of **5c** and performed the reaction in the absence of heating under catalysis by Sc(OTf)$_3$, because this catalyst worked well for the first cycloaddition of **1** and DMAD. In this case, reaction of **4** (1 equiv) and DBA (1 equiv) in the presence of Sc(OTf)$_3$ (25% mol) in dichloromethane at room temperature for 5 min gave **5c** (63%) after column chromatography with no traces of **6a**. Although in this case the new conditions gave satisfactory yield, in other cases there was little difference in the results given by the thermal cycloaddition or by the reaction under catalysis. Thus, the reaction of **4** (1 equiv) and DMAD (2.5 equiv) in the presence of Sc(OTf)$_3$ (50% mol) in dichloromethane at room temperature for 15 min gave **5a** (82%) in practically the same yield obtained under thermal conditions.

We did not observe traces of the expectable 1:2 adducts of **4** plus two molecules of DMAD or DCA in their respective reactions. In addition, compounds **5a** and **5b** did not react with a large excess of DBA in refluxing chlorobenzene for 4 h but were recovered unchanged from the reaction residues. The addition of Sc(OTf)$_3$ (50% mol) to the latter reactions did not modify the results. Nevertheless, the reaction of **5c** (1 equiv) with excess DMAD (1.5 equiv) in refluxing chlorobenzene for 4 h gave the new adduct **6b**, as a yellow product (mp 91−92 °C, 83%) (Scheme 2). In conclusion, the stepwise additions of **4** and two molecules of dipolarophile were possible for **4** + 2DBA or [**4** + DBA] + DMAD. The presence of the nonaromatic 1,4-thiazine fused to the 1,2-dithiole-3-thione in **4**, in contrast to the aromatic pyrrole in **1**,

SCHEME 3



makes the dithiolothione **4** more reactive than **1** in reactions with acetylene dipolarophiles but also makes the 1:1 adducts of **4** less reactive for a second cycloaddition, because of the presence of the dithiolactone formed during the first cycloaddition. The presence of benzoyl groups in the starting acetylenes favors the first and the second cycloaddition of **4**, probably because these groups enhance the electronic delocalization in the transition states and thus facilitate the formation of products.

To expand the scope of this synthetic pathway, we performed new cycloadditions to other activated acetylenes. Acetylenedicarbaldehyde diethyl acetal[16] (ACDA), a precursor of the unstable acetylenedicarbaldehyde,[17] has been used in thermal cycloadditions to monocyclic dithiolethiones.[18] Under catalysis, the reaction of **4** (1 equiv) and ACDA (2 equiv) in the presence of Sc(OTf)$_3$ (50% mol), in dichloromethane at room temperature for 10 min, gave a solid product that was hydrolyzed in formic acid at 60 °C for 30 min, to give the 1:1 cycloadduct 4,5-diformyl-1,3-dithiol-2-ylidenyl[1,2]dithiolo[1,4]thiazine **5d**, as a red solid (mp 76−77 °C, 83%) with no traces of other products (Scheme 3). Compound **5d** was easily characterized by spectroscopy and microanalysis. Its ^{1}H NMR spectrum showed two formyl protons, one methyl group and two diastereotopic methylenic protons showed as two groups of six signals, every group of six signals consisting of two quartets. As in previous cases, these signals indicate the presence of conformers, which is rather unexpected in a compound with so simple structure, but the presence of this complex methylene group in ^{1}H NMR is a characteristic of all cycloadducts with the [1,4]thiazine ring in their structure.

Products **5a**−**d** have structures that include many electron-donor and -acceptor groups that make them interesting as building blocks for organic new materials. A combination of the conjugated 1,3-dithiole with furan or thiophene rings could lead to polyfuran[19] or polythiophene[20] derivatives of interest as conducting polymeric materials.[21] We therefore prepared the polyhet-

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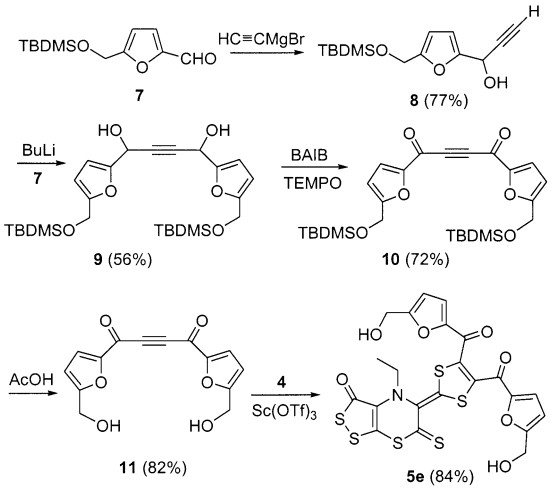
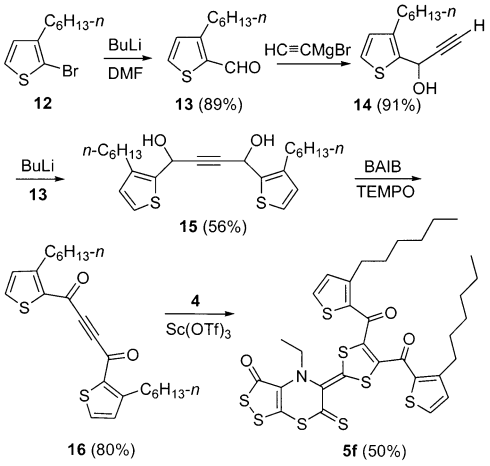
SCHEME 4



SCHEME 5

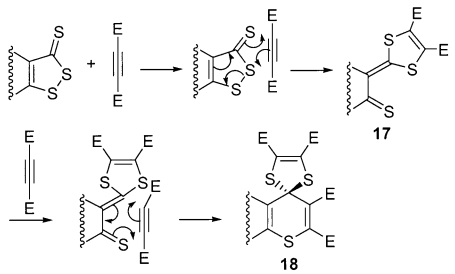


erocyclic diol **5e** in five steps from 5-*tert*-butyldimethylsilyloxymethyl-2-furylcarbaldehyde[22] **7** (Scheme 4).

The reaction of **7** and ethynylmagnesium bromide gave the furylpropynol **8** (77%) that reacted with butyllitium and then **7** to give diol **9** (56%). This diol **9** was successively oxidized with (bisacetoxyiodo)benzene (BAIB) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)[23] to give diketone **10** (72%) and deprotected with water−acetic acid to give **11** (82%). Cycloaddition of dithiolethione **4** (1 equiv) and difuroylacetylene **11** (1.2 equiv) in the presence of $Sc(OTf)_3$ successfully gave the 1:1 cycloadduct **5e** as a red solid, mp 134−135 (84%). Following a closely related pathway,[24] we synthesized the conjugated dithiophene **5f** in five steps from 2-bromo-3-hexylthiophene[25] **12** (Scheme 5).

Reaction of **12** with butyllithium and then dimethylformamide (DMF) gave the thiophenecarboxaldehyde **13** (89%). Aldehyde **13** and ethynylmagnesium bromide gave

SCHEME 6



the thienylpropynol **14** (91%) that reacted with butyllithium and then **13** to give diol **15** (56%). This diol **15** was oxidized with (bisacetoxyiodo)benzene (BAIB) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)[23] to give diketone **16** (80%). Cycloaddition of dithiolethione **4** (1 equiv) and **16** (2 equiv) in the presence of $Sc(OTf)_3$ successfully gave the 1:1 cycloadduct **5f**, as a red solid (mp 58−59, 50%). Therefore, the reaction of the 1,2-dithiole-3-thione **4** and activated acetylenes, catalyzed by $Sc(OTf)_3$, constitutes a very mild and convenient procedure for the preparation of interesting heterocyclic diacyl 1,3-dithiol-2-yl derivatives of the [1,2]dithiolo[1,4]thiazine ring system.

Reaction Mechanism and Structural Study. Compounds **1** and **4** showed an unusual behavior in their respective cycloadditions with diacylacetylenes. The general mechanism of all these reactions involves a first cycloaddition of the 1,2-dithiol-3-thione groups to the triple bond (Scheme 6), to give cycloadducts **17**.

1,3-Dithioles such as **17** are reported to be stable compounds[8−10,14,15] that can react as heterodienes with a second molecule of dienophile to give bis-adducts **18**. In our case, the 1:1 adducts of **1** and the dipolarophiles were very reactive unsaturated thiones that quickly reacted with a second molecule of dienophile to give products in which the aromaticity of the pyrrole nucleus was again reached. Both facts favored the isolation of 1:2 cycloadducts of **1** and dienophiles as the final products. On the contrary, the 1:1 adducts of **4** and the same dipolarophiles were stable dithiolactones that did not react with a second molecule of dipolarophile, except for **5c**.

The [1,2]dithiolo[3,4-*b*][1,4]thiazine derivatives have a folded structure;[26] therefore, adducts **5a**−**f** (and also **6a**,**b**) are expected to be asymmetric, and this fact can be observed in their ^{1}H NMR spectra that show 12 signals corresponding to methylenic protons in every compound. A representative example is given in Figure 1. To measure the barriers to inversion of nitrogen, we registered the ^{1}H NMR spectra of **5a**, **5c**, and **6a** in deuterated chlorobenzene from room temperature to 125 °C, but in all cases we did not get the coalescence temperature within these limits. The evolution of methylenic signals in the ^{1}H NMR of **5a** is given in Figure 2. The two groups of six signals (each group is constituted by two quartets), which are separated by 0.40 ppm at room temperature, lose intensity and resolution when temperature increases, and at 125 °C only two broad singlets separated by 0.31 ppm remain. The coalescence temperature is

(22) McNelis, B. J.; Sternbach, D. D.; Macphail, A. T. *Tetrahedron* **1994**, *50*, 6767.

(23) (a) DeMico, A.; Margarita, R.; Parlanti, L.; Vescovi, A.; Piancatelli, G. *J. Org. Chem.* **1997**, *62*, 6974. (b) Barriga, S. *Synlett* **2001**, 563.

(24) For the related 1,4-dithiophen-2-ylbut-2-yne-1,4-dione, see: Skabara, P. J.; Serebryakov, I. M.; Roberts, D. M.; Perpichka, I. F.; Coles, S. J.; Hursthouse, M. B. *J. Org. Chem.* **1999**, *64*, 6418.

(25) Wang, F.; Rauh, R. D.; Rose, T. L. *J. Am. Chem. Soc.* **1997**, *119*, 11106.

(26) Barriga, S.; Fuertes, P.; Marcos, C. F.; Miguel, D.; Rakitin, O. A.; Rees, C. W.; Torroba, T. *J. Org. Chem.* **2001**, *66*, 5766.

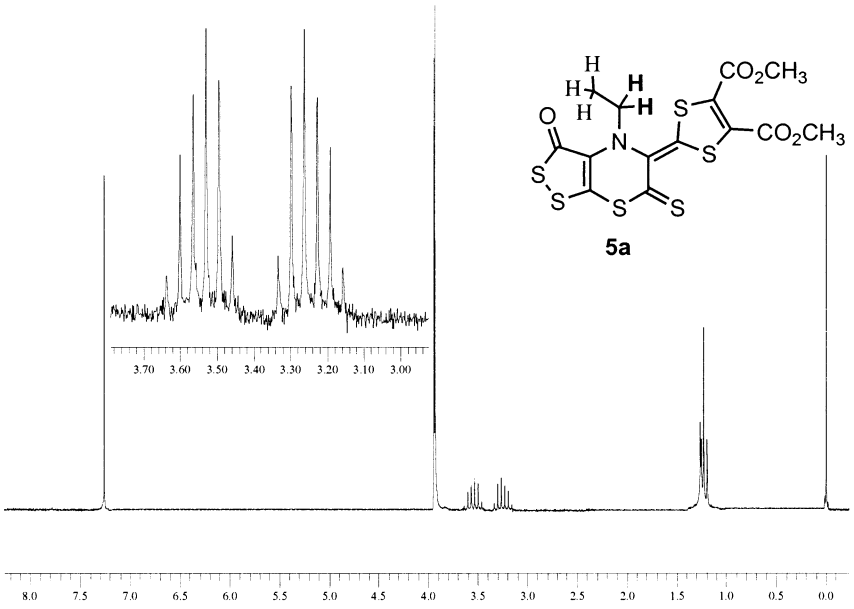


FIGURE 1. ^{1}H NMR spectrum of **5a** and amplification of the methylenic protons region.

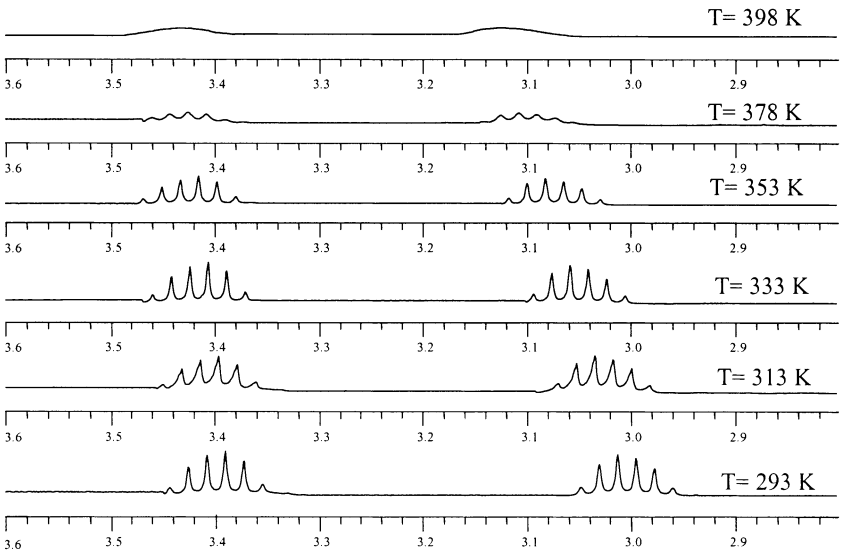


FIGURE 2. ^{1}H NMR spectra of the methylene region of **5a** registered at 293−398 K.

therefore beyond 125 °C, thus by applying the Eyring[27] equation to the system we obtained that the rotation barrier has to be higher than 79.68 kJ mol^{-1}.

Electrochemical Study. We performed cyclic voltammetry experiments of 5×10^{-4} M solutions of **5a** and **5f** in dichloromethane at 20 °C, using Bu_4NPF_6 as supporting electrolyte in an approximate 0.1 M concentration, a platinum ball as working electrode, platinum wire as an auxiliary electrode, and saturated calomelanes as reference electrode. The cyclic voltammograms were registered at different scanning velocities, showing irreversible processes for both **5a** and **5f**. The comparison between the intensities of the first oxidation and first reduction waves for **5a** and **5f** showed in both cases electronic transfers in which the same number of electrons was apparently involved in both the oxidation and reduction processes, although controlled potential electrolysis was not used to determine the number of implied electrons. The Figure 3 gives the cyclic voltammogram of **5a** registered at 100 mV/s. The oxidation peak potential appeared at $E_p^{ox} = 1.25$ V and the reduction peak potential appeared at $E_p^{red} = -1.00$ V. On the other hand, the cyclic voltammogram of **5f** registered at 100 mV/s showed in the first scan an irreversible oxidation at peak potential of 0.81 V. A cathodic peak appears at 0.55 V in the reverse scan (Figure 4). After several scans the waves at 0.81 and 0.55 V disappeared gradually, until the resulting voltammogram was similar to that obtained for **5a** (Figure 5). Then the voltammogram of **5f** remained unchanged after several scans and using freshly prepared working electrodes. The oxidation peak potential appeared at $E_p^{ox} = 1.20$ V and the reduction wave peak potential appeared at $E_p^{red} = -1.05$ V. This behavior can

(27) Friebolin H. in *Basic One- and Two-Dimensional NMR Spectroscopy*, 3rd ed.; Wiley-VCH: Weinheim, 1998; Chapter 11.

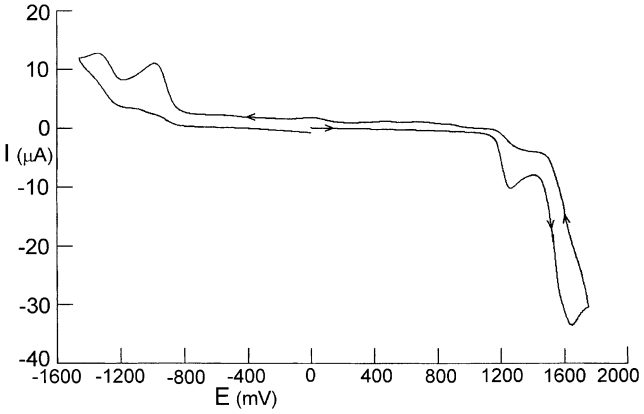


FIGURE 3. Cyclic voltammogram of **5a** registered in dichoromethane at room temperature.

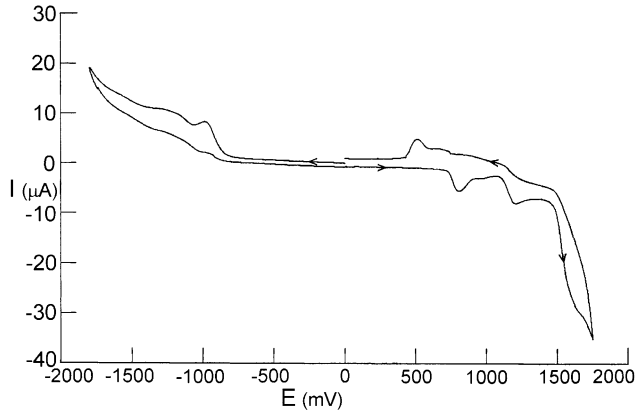


FIGURE 4. Cyclic voltammogram of **5f** (first scan) registered in dichloromethane at room temperature.

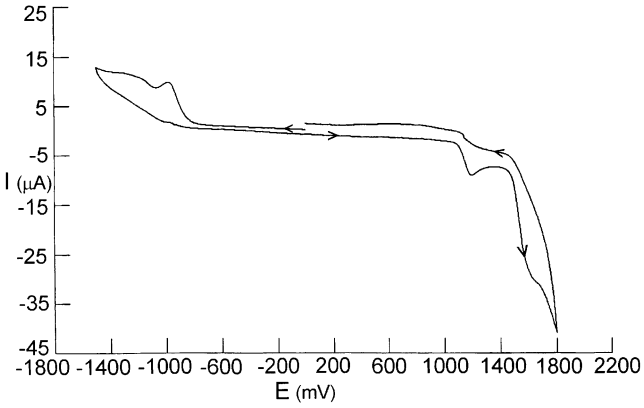


FIGURE 5. Cyclic voltammogram of **5f** registered after several scans.

be due to the existence of an electrochemically catalyzed process that follows the first electron transfers during the experiment. The final product in the electrochemical cell likely has a similar heterocyclic core to that of **5a**. Thus, the differences in the cyclic voltammograms can be attributed to the electrochemical activity of the thienyl groups.

Conclusion

We have shown that 1,3-dipolar cycloadditions of appropriate polycylic 1,2-dithiol-3-thiones and partially protected or unprotected diacyl acetylenes constitute a very fast way to get complex polyheterocyclic systems that are not easily available by other routes. Some of the new heterocyclic systems, obtained by this methodology, showed chiral conformers in ^{1}H NMR with high interconversion barriers and an electrochemical behavior, studied by cyclic voltammetry, that can be modified by electroactive groups, conferring to these compounds a promising future as new organic materials.

Experimental Section

Bis[1,2]dithiolopyrrole ketothione **1**[4b,5a] and bis[1,2]dithiolo-[1,4]thiazine ketothione **4**[4a,b] were prepared as described. Dicyanoacetylene[11] (DCA), dibenzoylacetylene[12] (DBA), acetylenedicarbaldehyde diethyl acetal[16] (ACDA), 5-*tert*-butyldimethylsilyloxymethyl-2-furylcarbaldehyde **7**,[22] and 2-bromo-3-hexylthiophene **12**[25] were prepared by following known methods. Dimethyl and diethyl acetylenedicarboxylate (DMAD and DEAD), scandium triflate [Sc(OTf)$_3$], ethynylmagnesium bromide, butyllithium, (bisacetoxyiodo)benzene (BAIB), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) were purchased and used without further purification. Aromatic and chlorinated solvents were distilled from phosphorus pentoxide. Melting points were not corrected. CH_2 and CH groups were identified by DEPT experiments on representative examples. Column chromatography was carried out on a medium-pressure liquid chromatography apparatus, with silica gel C60. Petroleum ether refers to the fraction bp 40−60 °C.

Tetramethyl3-Oxo-4-ethyl-5-spiro(1,3-dithiol-2-yl)[1,2]-dithiolo[3,4-*b*]thiopyrano[2′,3′-*d*]pyrrole-4″,5″,6,7-tetracarboxylate 2a. DMAD (123 μL, 142 mg, 1.00 mmol) was added to a solution of bis[1,2]dithiolopyrrole **1** (116 mg, 0.40 mmol) in toluene (15 mL). The resulting solution was stirred under reflux for 2 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (silica gel 60, petroleum ether to CH_2Cl_2–ethyl acetate 20:1) to give **2a**: yellow solid (CH_2Cl_2–petroleum ether) (150 mg, 65%); mp 218−220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.76 (q, J = 7.0 Hz, 2H, CH_2), 3.90 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 3.82 (s, 6H, 2·CH_3), 1.58 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.3 (*C*═O), 165.0 (*C*═O), 162.8 (*C*═O), 160.1 (*C*═O), 135.6, 129.9, 129.4, 129.0, 127.2, 125.8, and 104.7 (7 × sp^2 *tertiary* C), 64.0 (*quaternary* C), 54.0, 53.4, 53.3 and 52.9 (4 × *C*H$_3$), 42.8 (*C*H$_2$), 15.9 (*C*H$_3$); IR (KBr, cm^{-1}) n 2955, 1739 (C═O), 1703 (C═O), 1667 (C═O), 1573, 1430, 1249, 1208; MS (EI) *m*/*z* 575 (M$^+$, 13), 516 (M − 59, 35), 456 (5), 400 (25), 341 (13), 59 ($CO_2CH_3^+$, 100); HRMS, M$^+$ = 574.9505 $C_{20}H_{17}NO_9S_5$ requires 574.9507. Anal. Calcd for $C_{20}H_{17}NO_9S_5$: C, 41.73; H, 2.98; N, 2.43. Found: C, 41.90; H, 3.00; N, 2.41.

Tetraethyl 3-Oxo-4-ethyl-5-spiro(1,3-dithiol-2-yl)[1,2]-dithiolo[3,4-*b*]thiopyrano[2′,3′-*d*]pyrrole-4″,5″,6,7-tetracarboxylate 2b. DEAD (160 μL, 170 mg, 1.00 mmol) was added to a solution of bis[1,2]dithiolopyrrole 1 (116 mg, 0.40 mmol) in toluene (15 mL) and the resulting solution was stirred under reflux for 2 h and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2–ethyl acetate 20:1) gave **2b**: yellow solid (CH_2Cl_2−petroleum ether) (170 mg, 67%); mp 140−141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.75 (q, J = 7.0 Hz, 2H, CH_2), 4.38 (q, J = 7.2 Hz, 2H, CH_2), 4.32 (q, J = 7.1 Hz, 2H, CH_2), 4.25 (q, J = 7.1 Hz, 4H, 2 × CH_2), 1.58 (t, J = 7.0 Hz, 3H, CH_3), 1.36 (t, J = 7.2 Hz, 3H, CH_3), 1.35 (t, J = 7.1 Hz, 3H, CH_3), 1.30 (t, J = 7.1 Hz, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.3 (*C*═O), 164.6 (*C*═O), 162.4 (*C*═O), 159.6 (*C*═O), 135.5, 130.5, 129.3, 129.1, 127.3, 126.1, and 104.6 (7 × sp^2 *tertiary* C), 63.5 and 62.7 (2 × *C*H$_2$), 57.7 (*quaternary* C), 42.7 (*C*H$_2$), 15.9, 13.9, and 13.7 (3 × *C*H$_3$); IR (KBr, cm^{-1}) ν 2990, 1743 (C═O), 1729 (C═O), 1694 (C═O), 1665 (C═O), 1573, 1286, 1254, 1030; MS (EI) *m*/*z* 631 (M$^+$, 33), 586 (M − 45, 5), 558 (M − 73, 100), 428 (32), 369 (11), 354 (8), 328 (8); HRMS, M$^+$ = 631.0041 $C_{24}H_{25}NO_9S_5$ requires

631.0133. Anal. Calcd for $C_{24}H_{25}NO_9S_5$: C, 45.63; H, 3.99; N, 2.22. Found: C, 45.38; H, 3.76; N, 2.14.

4-Ethyl-5-spiro(4,5-dicyano-1,3-dithiol-2-yl)-6,7-dicyano-[1,2]dithiolo[4,3-*b*]thiopyrano[2′,3′-*d*]pyrrol-3-one 2c. DCA (36 mg, 0.474 mmol) was added to a solution of bis[1,2]-dithiolopyrrole **1** (55 mg, 0.189 mmol) in benzene (10 mL) and the resulting solution was stirred under reflux for 2 h and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2–ethyl acetate 90:10) gave **2c**, yellow solid (CH_2Cl_2–-petroleum ether) (31 mg, 38%), mp 228−229 °C. The low solubility of **2c** in common solvents and its slow decomposition upon standing in solution precluded the acquisition of its ^{13}C NMR spectrum: ^1H NMR ($CDCl_3$, 400 MHz) δ 4.71 (q, $J = 7.0$ Hz, 2H, CH_2), 1.60 (t, $J = 7.0$ Hz, 3H, CH_3); IR (KBr, cm^{-1}) ν 2222 (C≡N), 1662 (C═O), 1530, 1063, 914; MS (EI) *m*/*z* 443 (M^+, 32), 428 (M − 15, 14), 414 (M − 29, 12), 383 (M − 60, 11), 353 (12), 335 (90), 320 (27), 307 (38), 291 (12), 276 (35), 140 (22), 76 (14), 70 ($SCCN^+$, 100); HRMS, $M^+ = 442.9098$ $C_{16}H_5N_5OS_5$ requires 442.9083.

4-Ethyl-5-spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)-6,7-dibenzoyl[1,2]dithiolo[4,3-*b*]thiopyrano[2′,3′-*d*]pyrrol-3-one 2d. DBA (201 mg, 0.860 mmol) was added to a solution of bis-[1,2]dithiolopyrrole **1** (100 mg, 0.344 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 30 min and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2) gave **2d**: yellow solid (CH_2Cl_2–-petroleum ether) (191 mg, 73%); mp 242−244 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.71−7.19 (m, 20H, 4·C_6H_5), 5.00 (q, $J =$ 6.9 Hz, 2H, CH_2), 1.73 (t, $J = 6.9$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.2 (*C*═O), 191.2 (*C*═O), 186.6 (*C*═O), 179.3 (*C*═O), 138.8, 137.0, 136.1, 135.7, and 135.2 (5 × sp^2 *tertiary* C), 134.7, 133.8, and 133.5 (3 × *C*H aromatic, DEPT), 132.2 and 131.1 (2 × sp^2 *tertiary* C), 130.5 and 130.3 (2 × *C*H aromatic, DEPT), 129.7 and 129.3 (2 × sp^2 *tertiary* C), 128.9, 128.5 and 128.4 (3 × *C*H aromatic, DEPT), 104.7 (sp^2 *tertiary* C), 63.3 (*quaternary* C), 43.0 (*C*H_2, DEPT), 16.1 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 1660 (C═O), 1594, 1529, 1446, 1244, 689; MS (FAB^+) *m*/*z* 760 ($M^+ + 1$, 10), 654 ($M^+ - 105$, 1), 494 (2), 462 (3), 434 (3), 290 (38), 105 ($PhCO^+$, 43). Anal. Calcd for $C_{40}H_{25}NO_5S_5$: C, 63.22; H, 3.32; N, 1.84. Found: C, 63.33; H, 3.39; N, 1.82.

Dimethyl 3-Oxo-4-ethyl-5-(1,3-dithiol-2-ylidenyl)-6-thioxo[1,2]dithiolo[4,3-*b*]pyrrole-4′,5′-dicarboxylate 3: DMAD (24 mg, 0.17 mmol) was added to a solution of **1** (50 mg, 0.17 mmol) and $Sc(OTf)_3$ (42 mg, 0.085 mmol) in dichloromethane (5 mL) and the resulting solution was stirred under reflux in a warm water bath for 2 h. Workup was performed under protection against direct sunlight irradiation. The solvent was removed in the rotatory evaporator. Preparative TLC (silica gel 60, CH_2Cl_2–petroleum ether 1:1) of the resulting solid gave **3** (17 mg, 23%), mp 116−117 °C (dec). ^1H NMR ($CDCl_3$, 400 MHz) δ 4.64 (q, $J = 7.2$ Hz, 2H, CH_2), 4.01 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 1.36 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.8 (*C*═S), 183.5 (*C*═O), 159.7 and 158.7 (2 × *C*═O), 146.2, 144.4, 139.9, 139.6, 133.5, and 131.2 (6 × sp^2 *tertiary* C), 56.0 and 54.2 (2 × *C*H_3), 41.5 (*C*H_2), 16.5 (*C*H_3); UV (CH_2Cl_2, 2.3×10^{-4} M), λ_{max} (ϵ) 616 (818), 441 (1598), 383 (2122), 275 (5646); IR (KBr, cm^{-1}) ν 1731 (C═O), 1716 (C═O), 1658 (C═O), 1434, 1260 (C═S), 1148, 1093, 1069, 801; MS (EI) *m*/*z* 433 (M^+, 100), 291 (M − 141, 76), 286 (9), 207 (5); HRMS, $M^+ = 432.9241$ $C_{14}H_{11}NO_5S_5$ requires 432.9241.

Dimethyl 3-Oxo-4-ethyl-5-(1,3-dithiol-2-ylidenyl)-6-thioxo[1,2]dithiolo[3,4-*b*][1,4]thiazine-4′,5′-dicarboxylate 5a. Thermal Procedure. DMAD (57 μL, 66 mg, 0.462 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4** (60 mg, 0.186 mmol) in benzene (5 mL) and the resulting solution was stirred under reflux for 10 min and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2) gave **5a**: red solid (CH_2Cl_2−petroleum ether) (70 mg, 81%); mp 159−160 °C.

Catalyzed Procedure. DMAD (19 μL, 22 mg, 0.15 mmol) was added to a solution of **4** (20 mg, 0.062 mmol) and $Sc(OTf)_3$ (15 mg, 0.031 mmol) in dichloromethane (2 mL), and the resulting solution was stirred at room temperature for 15 min and worked up as before. Flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) gave **5a** (24 mg, 82%): ^1H NMR ($CDCl_3$, 400 MHz) δ 3.94 (s, 3H, CH_3), 3.92 (s, 3 H, CH_3), 3.51 (six signals, double quartet, $J = 14.4$ Hz, $J = 7.2$ Hz, 1H, $^1/_2$-CH_2), 3.25 (six signals, double quartet, $J = 14.4$ Hz, $J = 7.2$ Hz, 1H, $^1/_2CH_2$), 1.22 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.4 (*C*═S), 184.8 (*C*═O), 161.2 (*C*═O), 159.6 (*C*═O), 159.4, 153.3, 134.5, 133.0, 132.2, and 132.1 (6 × sp^2 *tertiary* C), 53.9 and 53.8 (2 × *C*H_3), 47.9 (*C*H_2), 13.4 (*C*H_3); IR (KBr, cm^{-1}) ν 1753 (C═O), 1714 (C═O), 1668 (C═O), 1436, 1295 (C═S), 1235, 710; MS (EI) *m*/*z* 465 (M^+, 38), 436 (M − 29, 100), 376 (5), 332 (8), 274 (38), 262 (8), 218 (8), 174 (12), 158 (15), 126 (40); HRMS, $M^+ = 464.8961$ $C_{14}H_{11}NO_5S_6$ requires 464.8962. Anal. Calcd for $C_{14}H_{11}NO_5S_6$: C, 36.12; H, 2.38; N, 3.01. Found: C, 36.12; H, 2.15; N, 2.93.

3-Oxo-4-ethyl-5-(4,5-dicyano-1,3-dithiol-2-ylidenyl)[1,2]-dithiolo[3,4-*b*][1,4]thiazine-6-thione 5b. DCA (30 mg, 0.39 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4** (50 mg, 0.15 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 10 min and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2) gave **5b**: red solid (CH_2Cl_2–petroleum ether) (42 mg, 68%); mp 173−175 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.60 (six signals, double quartet, $J = 14.2$ Hz, $J = 7.1$ Hz, 1H, $^1/_2CH_2$), 3.21 (six signals, double quartet, $J = 14.2$ Hz, $J = 7.1$ Hz, 1H, $^1/_2CH_2$), 1.23 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6 (*C*═S), 184.4 (*C*═O), 154.3, 151.9, 133.8, and 131.8 (4 × sp^2 *tertiary* C), 119.8 (*C*≡N), 118.9 (*C*≡N), 108.8 and 108.3 (2 × sp^2 *tertiary* C), 48.2 (*C*H_2, DEPT), 13.4 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 2925, 2240 (C≡N), 1667 (C═O), 1640 (C═O), 1364, 1305 (C═S), 1000, 710; MS (EI) *m*/*z* 399 (M^+, 40), 370 (M − 29, 100), 310 (5), 266. (17), 234 (11), 208 (27), 76 (14), 70 (18); HRMS, $M^+ = 398.8750$ $C_{12}H_5N_3OS_6$ requires 398.8757. Anal. Calcd for $C_{12}H_5N_3OS_6$: C, 36.07; H, 1.26; N, 10.52. Found: C, 36.00; H, 1.36; N, 10.48.

3-Oxo-4-ethyl-5-(4,5-dibenzoyl-1,3-dithiol-2-ylidenyl)-[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 5c. Thermal Procedure. DBA (24 mg, 0.10 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4** (30 mg, 0.09 mmol) in benzene (10 mL) and the resulting solution was stirred under reflux for 5 min and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2–ethyl acetate 90:10) gave **5c**: red solid (CH_2Cl_2–petroleum ether) (25 mg, 48%); mp 78−79 °C.

Catalyzed Procedure. DBA (40 mg, 0.17 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4** (55 mg, 0.17 mmol) and $Sc(OTf)_3$ (21 mg, 0.043 mmol) in dichloromethane (2 mL); the resulting solution was stirred at room temperature for 5 min and worked up as before. Flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) gave **5c** (61 mg, 63%): ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50−7.44 (m, 5H, C_6H_5), 7.29−7.22 (m, 5H, C_6H_5), 3.59 (six signals, double quartet, J = 14.2 Hz, $J = 7.1$ Hz, 1H, $^1/_2CH_2$), 3.34 (six signals, double quartet, $J = 14.2$ Hz, $J = 7.1$ Hz, 1H, $^1/_2CH_2$), 1.27 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.3 (*C*═S), 186.7 (*C*═O), 184.7 (*C*═O), 161.6, 153.1, 141.6, 140.3, 136.7, and 136.4 (6 × sp^2 *tertiary* C), 134.3, 134.2, 134.0, and 133.9 (4 × *C*H aromatic, DEPT), 132.2 and 132.0 (2 × sp^2 *tertiary* C), 128.9 and 128.7 (2 × *C*H aromatic, DEPT), 48.6 (*C*H_2, DEPT), 13.5 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 2960, 2923, 1657 (C═O), 1597, 1448, 1261 (C═S), 1049, 695; MS (EI) *m*/*z* 557 (M^+, 12), 542 (M − 15, 4), 528 (M − 29, 33), 513 (M − 44, 8), 501 (M − 56, 3), 452 (M − 105, 3), 351 (12), 162 (14), 105 ($PhCO^+$, 100), 77 (Ph^+, 58); HRMS, $M^+ = 556.9376$ $C_{24}H_{15}NO_3S_6$ requires 556.9282. Anal. Calcd for $C_{24}H_{15}NO_3S_6$: C, 51.68; H, 2.71; N, 2.51. Found: C, 51.75; H, 2.88; N, 2.74.

4-Ethyl-5-spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)-6,7-dibenzoyl[1,2]dithiolo[4,3-*b*]thiopyrano[2′,3′-*d*][1,4]-thiazin-3-one 6a. DBA (54 mg, 0.23 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4** (30 mg, 0.09 mmol) in benzene (10 mL), and the resulting solution was stirred

under reflux for 30 min and worked up as for **2a**. MPLC (silica gel 60, petroleum ether to CH_2Cl_2) gave **6a**: yellow solid (CH_2Cl_2–petroleum ether) (54 mg, 73%); mp 104−106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69−7.19 (m, 20H, 4 × C_6H_5), 3.97 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2$-CH_2), 3.82 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.44 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) d 192.7, 189.6, 187.7, 186.5, and 182.6 (5 × *C*═O), 155.7, 140.6, 138.5, 137.7, 137.4, 137.3, 136.8, 136.7, 136.1, 135.0, and 134.9 (11 × sp^2 *tertiary* C), 134.6, 134.2, 133.7, 133.4, 133.1, 129.9, 129.6, 129.1, and 128.8 (9 × *C*H aromatic, DEPT), 128.6 (sp^2 *tertiary* C), 128.4 and 128.2 (2 × *C*H aromatic, DEPT), 121.5 (sp^2 *tertiary* C), 70.8 (*quaternary* C), 50.2 (*C*H_2, DEPT), 13.4 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 1660 (C═O), 1595, 1532, 1447, 1257, 689; MS (FAB$^+$) *m*/*z* 792 (M$^+$ + 1, 2), 686 (M − 105, 1), 549 (1), 521 (1), 147 (25), 105 (PhCO$^+$, 33). Anal. Calcd for $C_{40}H_{25}NO_5S_6$: C, 60.66; H, 3.18; N, 1.77. Found: C, 60.58; H, 3.26; N, 1.65.

Dimethyl 3-Oxo-4-ethyl-5-spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)[1,2]dithiolo[4,3-*b*]thiopyrano[2′,3′-*d*][1,4]thiazine-6,7-dicarboxylate 6b. DMAD (15 mL, 17 mg, 0.121 mmol) was added to a solution of dibenzoyl[1,3]dithiolylidenyl[1,2]-dithiolo[1,4]thiazine **5c** (45 mg, 0.081 mmol) in chlorobenzene (5 mL), and the resulting solution was stirred under reflux for 4 h. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1 to CH_2Cl_2–ethyl acetate 5:1) to give 6b: yellow solid (CH_2Cl_2–petroleum ether) (47 mg, 83%); mp 91−92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (dd, J = 8.4 Hz, J = 2.0 Hz, 4H, aromatic H), 7.42 (dt, J = 8.4 Hz, J = 2.4 Hz, 2 H, aromatic H), 7.26 (dt, J = 7.6 Hz, J = 2.4 Hz, 4H aromatic H), 3.90 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 3.76 (double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 3.67 (double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.30 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.4, 187.1, 182.9, 168.6 and 161.0 (5 × *C*═O), 154.9, 143.9, 138.8, 137.4, 137.3, 137.2, 136.3, and 134.5 (8 × sp^2 *tertiary* C), 133.3 and 133.2 (2 × *C*H aromatic), 130.9 and 129.7 (2 × sp^2 *tertiary* C), 128.8, 128.6, 128.4, and 128.3 (4 × *C*H aromatic), 67.1 (*quaternary* C), 54.3 and 52.9 (2 × *C*H_3), 51.0 (*C*H_2), 12.7 (*C*H_3); IR (KBr, cm^{-1}) ν 2951, 2923, 1713 (C═O), 1651 (C═O), 1435, 1258, 1111, 1017, 693; MS (FAB$^+$) *m*/*z* 700 (M + 1, 10), 641 (M − 59, 11), 369 (8), 307 (13), 154 (65), 105 (PhCO$^+$, 79). Anal. Calcd for $C_{30}H_{21}NO_7S_6$: C, 51.48; H, 3.02; N, 2.00. Found: C, 51.34; H, 2.96; N, 1.80.

3-Oxo-4-ethyl-5-(4,5-diformyl-1,3-dithiol-2-ylidenyl)-[1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 5d. ACDA[16] (72 mg, 0.462 mmol) was added to a solution of bis[1,2]dithiolo-[1,4]thiazine **4** (75 mg, 0.232 mmol) and Sc(OTf)$_3$ (57 mg, 0.116 mmol) in dichloromethane (2 mL), and the resulting solution was stirred at room temperature for 10 min. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (silica gel 60, CH_2Cl_2–petroleum ether 3:1 to CH_2Cl_2) to give a red solid (CH_2Cl_2–petroleum ether) (92 mg). Then the red solid was dissolved in formic acid and heated at 60 °C for 30 min. The mixture was left to reach room temperature and then poured on water (30 mL), the organic layer separated, and the aqueous layer extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The resulting solid was purified by flash chromatography (silica gel 60, CH_2Cl_2) to give **5d**: red solid (CH_2Cl_2) (78 mg, 83% overall); mp 76−77 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.42 (s, 2H, 2 CHO), 3.59 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 3.26 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 1.21 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) d 196.1 (*C*═S), 184.5, 180.0, and 179.2 (3 × *C*═O), 156.3, 152.0, 147.5, 146.1, 132.8, and 132.0 (6 × sp^2 *tertiary* C), 47.9 (*C*H_2), 13.4 (*C*H_3); IR (KBr, cm^{-1}) ν 2956, 2923, 2851, 1668 (C═O), 1653 (C═O), 1636 (C═O), 1261, 1103, 1075, 1047, 800. MS (EI) *m*/*z* 405 (M$^+$, 65), 376 (M − 29, 100), 348 (M − 58, 60), 186 (25), 149 (35), 71 (30); HRMS, M$^+$ = 404.8746 $C_{12}H_7NO_3S_6$ requires 404.8750. Anal. Calcd for: C, 35.54; H, 1.74; N, 3.45. Found: C, 35.46; H, 1.86; N, 3.59.

1-(5-*tert*-Butyldimethylsilyloxymethyl-2-furyl)prop-2-yn-1-ol 8. Ethynylmagnesium bromide (20.0 mL, 9.00 mmol, 0.45 M in THF) was added to a solution of 5-*tert*-butyldimethylsilyloxymethyl-2-furylcarbaldehyde[22] **7** (1.80 g, 7.50 mmol) in THF (10 mL) and the resulting solution was stirred at room temperature for 1 h. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the latter solution, the organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) to give **8**: yellow oil (1.54 g, 77%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.39 (d, J = 3.0 Hz, 1H, aromatic H), 6.18 (d, J = 3.0 Hz, 1H, aromatic H), 5.42 (s, br, 1H, CH), 4.62 (s, 2H, CH_2), 2.75 (s, br, 1H, OH), 2.59 (d, J = 2.0 Hz, 1H, C≡CH), 0.89 (s, 9H, 3 × CH_3), 0.08 (s, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 154.9 and 151.9 (2 × C aromatic), 108.6 and 107.9 (2 × *C*H aromatic), 81.0 (*C*≡CH), 73.9 (C≡*C*H), 58.2 (*C*H), 57.9 (*C*H_2), 25.8 (*C*H_3), 18.3 (*C*Si), −5.3 (*C*H_3Si); IR (neat, cm^{-1}) ν 3311 (OH), 2954, 2929, 2885, 2857, 1472, 1464, 1257, 1079, 838 (Si−C), 779 (Si−C).

1,4-Bis(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)-but-2-yne-1,3-diol 9. Butyllithium (5.2 mL, 8.32 mmol, 1.6 M in hexanes) was added to a stirred solution of 1-(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)prop-2-yn-1-ol **8** (996 mg, 3.74 mmol) in THF (5 mL) at −78 °C, and the resulting solution was stirred for 15 min. Then 5-*tert*-butyldimethylsilyloxymethyl-2-furylcarbaldehyde[22] **7** (898 mg, 3.74 mmol) was added and the resulting solution was left to reach room temperature and stirred for additional 30 min at room temperature. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic extracts were dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1 to CH_2Cl_2–ethyl acetate 17:3) to give **9**: brown oil (1.058 g, 56%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.38 (d, J = 3.0 Hz, 2H, 2 × CH aromatic), 6.18 (d, J = 3.0 Hz, 2H, 2 × CH aromatic), 5.49 (s, br, 2H, 2 × CH), 4.62 (s, 4H, 2 × CH_2), 0.89 (s, 9H, 3 × CH_3), 0.07 (s, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 154.9 and 151.9 (aromatic C), 108.7 and 107.9 (2 × *C*H aromatic), 83.0 (*CC*), 58.2 (*C*H), 58.1 (*C*H_2), 25.8 (*C*H_3), 18.4 (*C*Si), −5.3 (*C*H_3Si); IR (neat, cm^{-1}) ν 3433 (OH), 2955, 2930, 2858, 1257, 1101, 838 (Si−C), 779 (Si−C).

1,4-Bis(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)-but-2-yne-1,3-dione 10. (Bisacetoxyiodo)benzene (BAIB) (1.440 g, 4.47 mmol) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (64 mg, 0.41 mmol) were added to a solution of 1,4-bis(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)but-2-yne-1,3-diol **9** (1.025 g, 2.03 mmol) in CH_2Cl_2 (5 mL), and the resulting solution was stirred at room temperature for 2 h. Then, additional CH_2Cl_2 (5 mL) and a saturated aqueous solution of $Na_2S_2O_3$ (5 mL) were added to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic extracts were washed successively with a saturated aqueous solution of $NaHCO_3$ and a saturated aqueous solution of NaCl and dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) to give **10**: orange solid (CH_2Cl_2–petroleum ether) (734 mg, 72%); mp 97−98 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48 (d, J = 3.5 Hz, 2H, 2 × CH aromatic), 6.53 (d, J = 3.5 Hz, 2H, 2 × CH aromatic), 4.77 (s, 4H, 2 × CH_2), 0.94 (s, 18H, 6 × CH_3), 0.13 (s, 12H, 4 × CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 162.8 (*C*═O), 161.9, 151.4, 124.2, and 109.7 (4 × *C*H aromatic), 82.9 (*C*≡*C*), 58.4 (*C*H_2), 25.5 (*C*H_3), 18.0 (*C*Si), −5.7 (*C*H_3Si); IR (neat, cm^{-1}) ν 2956, 2930,

2857, 1643 (C═O), 1633 (C═O), 1513, 1372, 1312, 1207, 1123, 1084, 1022, 848, 777.

1,4-Bis(5-hydroxymethyl-2-furyl)but-2-yne-1,4-dione 11. A solution of 1,4-bis(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)but-2-yne-1,3-dione **10** in acetic acid−THF−water 3:1:1 (10 mL) was heated under reflux for 2.5 h. Then, the solution was left to reach room temperature, poured on water (20 mL), and extracted with CH_2Cl_2 (4 × 20 mL). The combined organic extracts were successively washed with a saturated aqueous solution of $NaHCO_3$ (10 mL) and water (10 mL) and dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, ethyl acetate) to give **11**: orange solid (ethyl acetate) (47 mg, 82%); mp 86−87 °C; ^{1}H NMR (CD_3COCD_3, 200 MHz) δ 7.68 (d, J = 2.6 Hz, 2H, 2 × CH aromatic), 6.68 (d, J = 2.6 Hz, 2H, 2 × CH aromatic), 4.73 (t, J = 5.0 Hz, 4H, 2 × CH_2); ^{13}C NMR (CD_3COCD_3, 50 MHz) δ 165.8 (*C*═O), 153.6 and 151.4 (2 × *C* aromatic), 126.5 and 112.1 (2 × *C*H aromatic), 84.2 (*C*≡*C*), 58.6 (*C*H_2); IR (KBr, cm^{-1}) ν 3426 (OH), 1626 (C═O), 1511, 1203, 1126, 421.

3-Oxo-4-ethyl-5-[4,5-bis(5-hydroxymethyl-2-furoyl)-1,3-dithiol-2-ylidenyl][1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 5e. 1,4-Bis(5-hydroxymethyl-2-furyl)but-2-yne-1,4-dione **11** (41 mg, 0.15 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4** (40 mg, 0.124 mmol) and Sc(OTf)$_3$ (30 mg, 0.06 mmol) in dichloromethane (2 mL), and the resulting solution was stirred at room temperature for 10 min. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by flash chromatography (silica gel 60, CH_2Cl_2–ethyl acetate 1:1) to give **5e**: red solid (CH_2Cl_2–ethyl acetate) (62 mg, 84%); mp 134−135 °C; ^{1}H NMR (CD_3COCD_3, 400 MHz) δ 7.42 (d, J = 3.7 Hz, 1H, aromatic H), 7.37 (d, J = 3.7 Hz, 1H, aromatic H), 6.54 (d, J = 3.7 Hz, 1H, aromatic H), 6.53 (d, J = 3.7 Hz, 1H, aromatic H), 4.67 (s, br, 2H, 2 × OH), 4.52 (t, J = 5.0 Hz, 4H, 2 × CH_2), 3.54 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 3.37 (six signals, double quartet, J = 14.4 Hz, J = 7.2 Hz, 1H, $^1/_2CH_2$), 0.94 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (CD_3COCD_3, 100 MHz) δ 193.3 (*C*═S), 186.1, 173.6, and 173.5 (3 × *C*═O), 165.0, 164.8, 164.4, 155.1, 152.0, 151.8, 142.3, 141.2, 134.0, and 133.5 (10 × sp^2 *tertiary* and aromatic C), 124.9, 124.7, 112.0, and 111.9 (4 × *C*H aromatic), 58.4 (*C*H_2), 49.5 (*C*H_2), 14.7 (*C*H_3); IR (KBr, cm^{-1}) ν 3426 (OH), 2924, 1656 (C═O), 1639 (C═O), 1631 (C═O), 1513, 1414, 1285, 1261, 1046, 1036; MS (EI) *m*/*z* 582 (M − CH_3, 5), 329 (12), 289 (8), 242 (9).

3-Hexylthiophene-2-carbaldehyde 13. Butyllithium (3.64 mL, 5.83 mmol, 1.6 M in hexanes) was added to a stirred solution of 2-bromo-3-hexylthiophene[25] **12** (1.20 g, 4.86 mmol) in THF (5 mL) at −78 °C and the resulting solution was stirred for 15 min. Then, dimethylformamide (710 mg, 0.75 mL, 9.72 mmol) was added and the resulting solution was left to reach room temperature and stirred for additional 30 min at room temperature. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL), the combined organic extracts were dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:3) to give **13**: yellow oil (847 mg, 89%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.04 (s, 1H, CHO), 7.64 (d, J = 5.0 Hz, 1H, CH aromatic), 7.00 (d, J = 5.0 Hz, 1 H, CH aromatic), 2.96 (t, J = 7.6 Hz, 2H, CH_2), 1.66 (m, 2H, CH_2), 1.31 (m, 6H, 3 × CH_2), 0.87 (t, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 181.7 (*C*HO), 152.4 and 137.3 (aromatic C), 134.0 and 130.4 (2 × *C*H aromatic), 31.2, 31.0, 28.6, 28.1, and 22.2 (5 × *C*H_2), 13.7 (*C*H_3); IR (neat, cm^{-1}) ν 2958, 2925, 2849, 1657 (C═O), 1432, 1237, 672; MS (EI) *m*/*z* 196 (M$^+$, 60), 139 (M − 57, 100), 126 (70), 97 (35).

1-(3-Hexyl-2-thienyl)prop-2-yn-1-ol 14. Ethynylmagnesium bromide (8.3 mL, 3.74 mmol, 0.45 M en THF) was added to a solution of 3-hexylthiophene-2-carbaldehyde **13** (490 mg, 2.50 mmol) in THF (5 mL) and the resulting solution was stirred at room temperature for 1 h. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the latter solution, the organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) to give **14**: deep yellow oil (504 mg, 91%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20 (d, J = 5.0 Hz, 1H, CH aromatic), 6.86 (d, J = 5.0 Hz, 1H, CH aromatic), 5.68 (s, br, 1H, CH), 2.64 (m, 3H, CH_2 and CCH), 1.61 (m, 2H, CH_2), 1.31 (m, 6H, 3 × CH_2) y 0.90 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 140.6 and 136.5 (2 × C aromatic), 129.1 and 124.3 (2 × *C*H aromatic), 84.2 (*C*≡CH), 73.9 (C≡*C*H), 58.0 (*C*H), 31.6, 30.6, 29.1, 28.2, and 22.5 (5 × *C*H_2), 14.0 (*C*H_3); IR (neat, cm^{-1}) ν 3307 (OH), 3289 (OH), 2954, 2924, 2855, 1674, 1661, 1464, 1028, 659.

1,4-Bis(3-hexyl-2-thienyl)but-2-yne-1,4-diol 15. Butyllithium (3.1 mL, 4.96 mmol, 1.6 M in hexanes) was added to a stirred solution of 1-(3-hexyl-2-thienyl)prop-2-yn-1-ol **14** in THF (5 mL) at −78 °C and the resulting solution was stirred for 15 min. Then, 3-hexylthiophene-2-carbaldehyde **13** (441 mg, 2.25 mmol) was added and the resulting solution was left to reach room temperature and stirred for additional 30 min at room temperature. An aqueous saturated solution of NH_4Cl (5 mL) was then added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL), the combined organic extracts were dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1 to CH_2Cl_2–ethyl acetate 19:1) to give **15**: brown oil (531 mg, 56%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.21 (d, J = 5.0 Hz, 2H, aromatic H), 6.87 (d, J = 5.0 Hz, 2H, aromatic H), 5.70 (m, 2H, 2 × CH), 2.65 (t, J = 6.0 Hz, 4H, 2 × CH_2), 1.61 (m, 4H, 2 × CH_2), 1.31 (m, 12H, 6 × CH_2), 0.90 (t, J = 6.5 Hz, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 140.7 and 136.5 (2 × C aromatic), 129.2 and 124.3 (2 × *C*H aromatic), 83.2 (*CC*), 58.1 (*C*H), 31.6, 30.6, 29.1, 28.3, 22.5 (5 × *C*H_2), 14.0 (*C*H_3); IR (neat, cm^{-1}) ν 3425 (OH), 3352 (OH), 2955, 2926, 2856, 1633, 1465, 1264, 1003, 738, 704.

1,4-Bis(3-hexyl-2-thienyl)but-2-yne-1,4-dione 16. (Bis-acetoxyiodo)benzene (BAIB) (355 mg, 1.10 mmol) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (16 mg, 0.10 mmol) were added to a solution of 1,4-bis(3-hexyl-2-thienyl)but-2-yne-1,4-diol **15** (209 mg, 0.50 mmol) in CH_2Cl_2 (2 mL) and the resulting solution was stirred at room temperature for 2 h. Then, additional CH_2Cl_2 (5 mL) and a saturated aqueous solution of $Na_2S_2O_3$ (5 mL) were added to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic extracts were washed successively with a saturated aqueous solution of $NaHCO_3$ and a saturated aqueous solution of NaCl and dried (Na_2SO_4), the solvent was removed in the rotatory evaporator, and the resulting residue was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) to give **16**: deep yellow oil (167 mg, 80%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.57 (d, J = 5.0 Hz, 2H, aromatic H), 7.01 (d, J = 5.0 Hz, 2H, aromatic H), 3.05 (t, J = 7.4 Hz, 4H, 2 × CH_2), 1.61 (m, 4H, 2 × CH_2), 1.30 (m, 12H, 6 × CH_2), 0.87 (t, J = 6.6 Hz, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.8 (*C*═O), 152.4 and 136.5 (aromatic C), 133.9 and 131.8 (2 × *C*H aromatic), 81.5 (*C*≡*C*), 31.6, 30.2, 30.1, 29.1, and 22.5 (5 × *C*H_2), 14.0 (*C*H_3); IR (neat, cm^{-1}) ν 3102 (OH), 2955, 2926, 2856, 1627 (C═O), 1515, 1409, 1279, 1242; MS (EI) *m*/*z* 414 (M$^+$, 3), 344 (M − 70, 13), 273 (8), 247 (14), 219 (45), 176 (100), 163 (29), 151 (54), 97 (25).

3-Oxo-4-ethyl-5-[4,5-bis(3-hexyl-2-thiophenecarbonyl)-1,3-dithiol-2-ylidenyl][1,2]dithiolo[3,4-*b*][1,4]thiazine-6-thione 5f. 1,4-Bis(3-hexyl-2-thienyl)but-2-yne-1,4-dione **16** (77 mg, 0.186 mmol) was added to a solution of bis[1,2]dithiolo-[1,4]thiazine **3** (30 mg, 0.093 mmol) and Sc(OTf)$_3$ (23 mg, 0.047

mmol) in dichloromethane (2 mL), and the resulting solution was stirred at room temperature for 10 min. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by flash chromatography (silica gel 60, CH_2Cl_2–petroleum ether 1:1) to give **5f**: red solid (CH_2Cl_2–petroleum ether) (34 mg, 0.046 mmol); mp 58−59 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, J = 5.0 Hz, 2H, aromatic H), 6.91 (two independent doublets, J = 5.0 Hz, 2H, aromatic H), 3.57 (six signals, double quartet, J = 14.2 Hz, J = 7.1 Hz, 1H, $^1/_2CH_2$), 3.31 (six signals, double quartet, J = 14.2 Hz, J = 7.1 Hz, 1H, $^1/_2CH_2$), 2.72 (quartet, J = 7.2 Hz, 4H, 2 × CH_2), 1.43 (m, 4H, 2 × CH_2), 1.25 (m, 12H, 6 × CH_2), 0.87 (m, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.5 (*C*=S), 184.6 (*C*=O), 177.9 (*C*=O), 177.8 (*C*=O), 162.0, 153.6, 153.3, 153.2, 142.4, 141.3, 134.0 and 133.8 (8 × sp^2 *tertiary* C), 133.5 and 133.2 (2 × *C*H aromatic), 132.2 and 131.8 (2 × sp^2 *tertiary* C), 131.6 and 131.5 (2 × *C*H aromatic), 47.8, 31.6, 30.1, 30.1, 29.1 and 22.6 (6 × *C*H_2), 14.1 and 13.4 (2 × *C*H_3); IR (KBr, cm^{-1}) ν 2952, 2924, 2852, 1672 (C=O), 1666 (C=O), 1630 (C=O), 1407, 1237. MS (FAB$^+$) m/z 738 (M + 1, 10), 307 (25).

Acknowledgment. We thank to Prof. Charles W. Rees, Chemistry Department, Imperial College of Science, Technology and Medicine, London (U.K.), for his helpful advice and to Dr. Gabriel García-Herbosa, Departamento de Química, Universidad de Burgos, for assistance in the electrochemical study. We gratefully acknowledge financial support from the Dirección General de Investigación of Spain (Project ref. BQU2001-0258 and grant no. FP97-08858491) and the Junta de Castilla y León, Consejería de Educación y Cultura, y Fondo Social Europeo (Project ref. BU07/00B).

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of products **5a**−**f** and **6a**,**b**, which show conformers due to restricted inversion of nitrogen, and of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020015A