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Synthesis of Highly Branched Sulfur−Nitrogen Heterocycles by Cascade Cycloadditions of [1,2]Dithiolo[1,4]thiazines and [1,2]Dithiolopyrroles

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We report the synthesis of some new polysulfur−nitrogen heterocycles by cascade cycloadditions to readily available polycyclic 1,2-dithiole-3-thiones. Thus, treatment of bis[1,2]dithiolopyrrole dithione **1** with dimethyl acetylenedicarboxylate (DMAD) or dibenzoylacetylene (DBA) gave the 1:4 adducts **2a**,**b** and **3a**. On the other hand, cycloaddition of bis[1,2]dithiolo[1,4]thiazine dithiones **4a**−**d** with the same dipolarophiles gave the 1:2, 1:3, or 1:4 adducts **5a**−**c**, **6a**, **7a**, **8a**, **9a**, and **10a**,**c**,**d** selectively in fair to high yields. Reaction conditions were crucial for achievement of selectivity in thermal reactions. Catalysis by scandium triflate was used in the reaction of **4a** and 2 equiv of DMAD. Treatment of the [1,2]dithiolo[1,4]thiazine dithione **11** with DBA gave the 1:2, 1:3 (two isomers), and 1:4 adducts **12**−**14** and **15a**−**d** selectively. Cyclic voltammetry of selected examples showed irreversible processes that were not influenced by peripheral groups bonded to the heterocyclic system.

Introduction

The prevention of cancer is an urgent and promising direction of biological research. Oltipraz [5-(2-pyrazinyl)-4-methyl-1,2-dithiole-3-thione] is considered one of the most promising chemopreventive agents on the basis of the results of preclinical studies and preliminary clinical trials.[1] It provides significant protection from tumorigenesis in hepatocellular, mammary, colon, and lung tumor models, and it induces resistance to many types of carcinogens including aflatoxin B1, a well-known hepatocellular carcinogen, by activating phase II carcinogen-detoxifying enzymes.[2] 3*H*-1,2-Dithiole-3-thione also protects against neoplasia.[3] These findings encouraged research in dithiolethiones[4] to develop related and unrelated compounds directed toward the same mechanism. Other dithiole derivatives are also studied as leads in anticancer research. The natural antibiotic leinamycin, possessing an unusual 1,3-dioxo-1,2-dithiolane ring, exhibits potent activity against murine experimental tumor leukemia P388 and sarcoma 180 and causes single-stranded DNA cleavage in vitro in the presence of thiols as activating reagents.[5] This makes leinamycin and its derivatives good anticancer drug candidates.[6]

We have developed fast methods for the synthesis of bis[1,2]dithiolo[1,4]thiazines,[7] bis[1,2]dithiolopyrroles,[8] a [1,2]dithiolo[1,4]thiazine,[9] mono- and bis[1,2]dithiolylamines,[10] and 1,2-dithiolodisulfides[11] that are also good starting materials for the preparation of more complex polyheterocyclic systems via 1,3-dipolar cycloadditions.[12] The three polycyclic dithiole derivatives of

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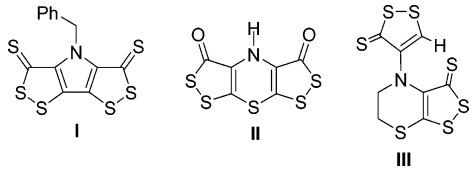


FIGURE 1.

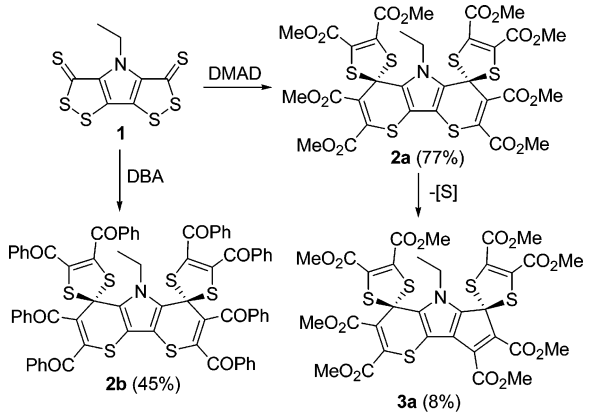
Figure 1 have been tested by the National Cancer Institute (NCI) at Bethesda in a disease-oriented in vitro anticancer screening program against 60 human tumor cell lines, showing moderate activity. The most active example **II** showed an LC50 of 4×10^{-5} M for some lines of leukemia and renal cancer and an LC50 of 5×10^{-5} M for some lines of CNS, melanoma, ovarian, and prostate cancer.

It was recently reported that fungicide chinomethionate, possessing a 1,3-dithiole-2-one as its reactive functionality, was the first member of a new family of photoinducible DNA-cleaving agents.[13] With the aim to obtain new polysulfur−nitrogen derivatives that could show increased antitumor activity, we wanted to prepare related compounds bearing multiple 1,3-dithiole groups. In this paper, we report the sequential reactions of [1,2]-dithiolopyrrole dithione **1**, bis[1,2]dithiolo[1,4]thiazine dithiones **4a**−**d**, and the [1,2]dithiolo[1,4]thiazine dithione **11**, with 2, 3, or 4 equiv of bis-activated alkynes, on the way to highly branched molecules with varied heterocyclic cores.

Results and Discussion

In a preliminary study, we reported that the bis[1,2]-dithiolopyrrole dithione **1** reacted with dimethyl acetylenedicarboxylate (DMAD) to give a complex polyadduct.[8a] Monocyclic 1,2-dithiol-3-thiones react with DMAD as classic 1,3-dipolar reagents,[14] but there are very few reported examples of multiple additions of DMAD to polycyclic bis-1,2-dithiole-3-thiones.[15] To understand the reactivity of heterocyclic dithiones, we first subjected the bis[1,2]dithiolopyrrole **1**, obtained in a one-pot reaction from commercial *N*-ethyldiisopropylamine and disulfur dichloride (S_2Cl_2),[7b] to reaction with three typical dipolarophiles. Thus, the reaction of **1** (1 equiv) and DMAD (5 equiv) in refluxing toluene for 3 h gave product **2a** (yellow solid, mp 224−226 °C, 77%) after chromatography as the main product (Scheme 1). Mass spectrometry and microanalysis showed **2a** to be the 1:4 adduct with the molecular formula $C_{32}H_{29}NO_{16}S_6$. In accordance with the symmetrical structure of **2a**, its ^{13}C NMR spectrum showed three carbonyl groups, five sp^2-tertiary carbon signals, one sp^3 quaternary carbon, two methoxy groups,

SCHEME 1



one methylene group, and one methyl group. Its ^{1}H NMR spectrum showed one methylene coupled to a methyl group and three methoxy singlets, one of them of double intensity, all consistent with the bis(spiro[1,3]dithiolo)-bisthiopyranepyrrole **2a**. A more polar colorful product **3a** was also separated by column chromatography as a mauve solid of mp 221−222 °C in very low yield (8%). In contrast with the simplicity of the spectral data of **2a**, the ^{1}H NMR spectrum of **3a** showed the methylene coupled to the methyl group and six methoxy singlets, two of them of double intensity, and its ^{13}C NMR spectrum showed six carbonyl groups, confirmed by the carboxyl absorptions in IR, 10 sp^2 tertiary carbons, one sp^3 quaternary carbon, five methoxy signals, one of them of much higher intensity, one methylene group, and one methyl group. We did not obtain the molecular peak in MS (FAB$^+$) spectroscopy, but the elemental analysis of **3a** was very close to that of **2a**, indicating that the structure of **3a** was closely related to **2a**, so we tentatively assigned to **3a** the structure of one sulfur extrusion from **2a**, which agreed with the available spectral and analytical data.

In the same way, the reaction of **1** (1 equiv) and dibenzoylacetylene[16] (DBA) (5 equiv) in refluxing benzene for 15 min gave **2b** (yellow solid, mp 140−142 °C, 45%) as the only product, which was characterized by spectroscopy and microanalysis. The presence of a quaternary C (δ 64) and an ethyl group (δ 44 and δ 17) in the ^{13}C NMR and in the ^{1}H NMR (a coupled quartet with a triplet at δ 5.7 and δ 2.1, respectively) spectra was a clear indication of the symmetry of structure **2b**. MS (FAB$^+$) and microanalysis of **2b** also agreed with a 1:4 adduct. On the other hand, treatment of **1** (1 equiv) with dicyanoacetylene[17] (5 equiv) in refluxing benzene for 30 min gave a new orange spot on TLC as the spot of **1** progressively faded, but the expected product decomposed during workup and could not be isolated. Therefore, the three dipolarophiles showed very different reactivity in their reactions with **1**, evidenced by the differences in the requisite temperature and time of every reaction, and in the stability of the final products. The less reactive

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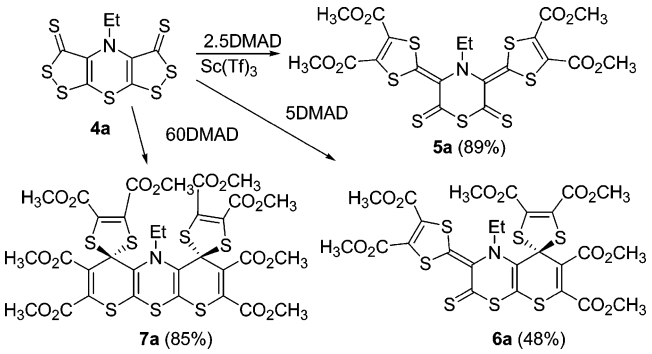
SCHEME 2

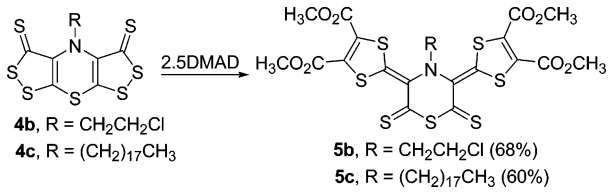


DMAD gave a higher yield than the more reactive DBA, and the most reactive DCA gave no stable product. Only 1:4 adducts were obtained with no traces of other adducts.

To expand the scope of the reaction, we then studied the cycloadditions of the bis[1,2]dithiolothiazine dithione **4a**[7b] with the activated acetylenes that previously gave stable products. In this way, the reaction of **4a** (1 equiv) with DMAD (2.5 equiv) in refluxing benzene for 10 min gave **5a** (orange solid, mp 119−120 °C, 44%) after chromatograpy, as the main product. MS (FAB^+) and microanalysis of **5a** gave a molecular formula $C_{20}H_{27}NO_8S_7$, that corresponded to a 1:2 adduct. ^1H and ^{13}C NMR spectra of **5a** showed an ethyl group, two different methyl esters, and one C═S group, confirmed by IR, in addition to four sp^2-tertiary carbon signals in the ^{13}C NMR spectrum, all suggesting a symmetric structure for **5a** (Scheme 2). Thus, the 3,5-bis(1,3-dithiol-2-ylidenyl)[1,4]-thiazine structure, with alternating dithiafulvene donor groups and a trithiacarboxylic anhydride, was assigned to **5a**.

In addition to **5a**, we separated, in yields lower than 5%, two minor compounds. Their MS spectra showed higher molecular weights that were temporarily assigned to the 1:3 (**6a**) and 1:4 (**7a**) cycloadducts. To solve the question, we looked for more selective conditions for the preparation of each compound and turned to milder conditions for the preparation of **5a** under Lewis acid catalysis. Effectively, the reaction of dithiolthione **4a** (1 equiv) with DMAD (2.5 equiv) in the presence of scandium triflate [$Sc(Tf)_3$, 25% mol] in CH_2Cl_2 at room temperature for 2 h gave **5a** (89%) as the only product. On the other hand, the reaction of **4a** (1 equiv) with a large excess of DMAD (60 equiv) in refluxing toluene for 9 h gave selectively **7a**, as a yellow solid of mp 58−59 °C (85%), purified by flash chromatography. The MS (FAB^+) spectrum of **7a** gave a molecular peak *m*/*z* 908 (M + 1), confirmed by microanalysis, indicating that we isolated the 1:4 adduct. The very simple ^1H NMR (only four types of methyl singlets in addition to the *N*-ethyl group) and ^{13}C NMR (17 peaks) spectra of **7a** were proof of the molecular symmetry for this high molecular weight compound, a new type of highly branched molecule. Finally, the reaction of **4a** with a lesser excess of DMAD (5 equiv) in refluxing benzene for 20 min gave the 1:3 adduct **6a** (orange solid, mp 87−88 °C, 48%) as the main product, but it was always accompanied by the 1:4 adduct **7a** in yields of 5−10%. Product **6a** was fully characterized by spectroscopy and microanalysis. The most striking feature was given by its ^1H NMR spectrum that showed,

SCHEME 3



in addition to five singlets assigned to methoxy groups and one triplet (the methyl group), two groups of six signals (each one constituted by two quartets), separated by 0.5 ppm at room temperature, in the aliphatic region. These groups of signals were assigned to diastereotopic methylene groups belonging to dynamic conformational isomers formed by restricted inversion of nitrogen in **6a**.

The facile 1:2 cycloaddition of bisdithiolothiazine dithiones and DMAD was extended to reactions of *N*-(2-chloroethyl)- and *N*-stearylbis[1,2]dithiolo[1,4]thiazines **4b**,**c**[9b,18] (1 equiv) with DMAD (2.5 equiv) in refluxing benzene for 20−45 min, that gave the corresponding 1:2 adducts **5b** (red solid, mp 178−179 °C, 68%) and **5c** (orange oily solid, 60%), whose structures were elucidated by spectroscopy and microanalysis (Scheme 3).

We then performed cycloadditions of dithiolothiazine **4a** and the expectedly more reactive DBA. Thus, the reaction of **4a** (1 equiv) with DBA (2.5 equiv) in refluxing benzene for 5 min gave a new product **8a** (orange solid, mp 115−116 °C, 67%) after chromatography, as the only reaction product. In addition to MS (FAB^+) and microanalysis, that clearly indicated that **8a** was the 1:2 adduct, the symmetry of the molecule is revealed in its simple ^1H NMR and ^{13}C NMR spectra. Furthermore, the reaction of **4a** (1 equiv) with DBA (5 equiv) in refluxing benzene for 15 min gave a mixture of **9a** (red solid, mp 115−116 °C, 26%) and **10a** (orange solid, mp 135−136 °C, 55%), which were separated by chromatography and characterized by spectroscopy and microanalysis. MS (FAB^+) and microanalyses clearly indicated that **9a** was the 1:3 adduct and **9b** was the 1:4 adduct, obtained as the main product. In addition, **9a** showed complex ^1H and ^{13}C NMR spectra, in comparison to the simpler ones obtained for the symmetric **10a**. We did not find a way to selectively synthesize the 1:3 adduct **9a** that was always obtained as the minor product. On the contrary, the reaction of **4a** (1 equiv) with an excess of DBA (12 equiv) in refluxing benzene for 2.5 h gave **10a** in high yield (95%) as the only reaction product (Scheme 4).

The *N*-ethyl group of these compounds worked as a probe of the molecular environment in ^1H NMR spectroscopy, which was useful to confirm structures **9a** and **10a**. Thus, the diastereoscopic methylene group of **9a** appeared as two groups of six signals (each one constituted by two quartets) separated by 0.36 ppm at room temperature, indicating, as for **6a**, the presence of asymmetric conformers due to restricted inversion of nitrogen. Furthermore, the methylene signal of tetra-adduct **10a** appeared as a broad singlet at room temperature, suggesting again the presence of conformational isomers.

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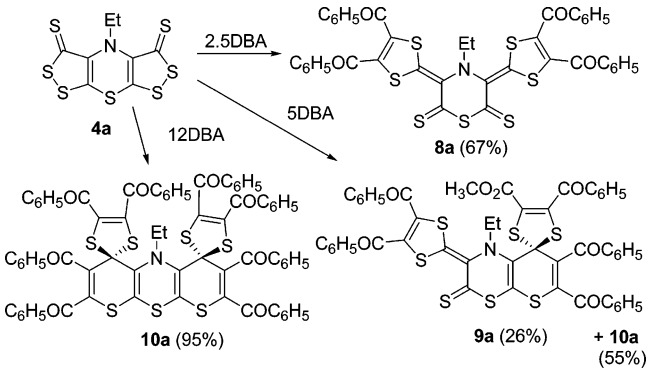
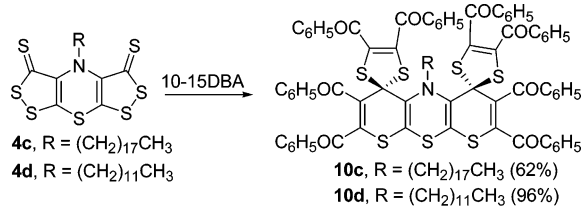
SCHEME 4



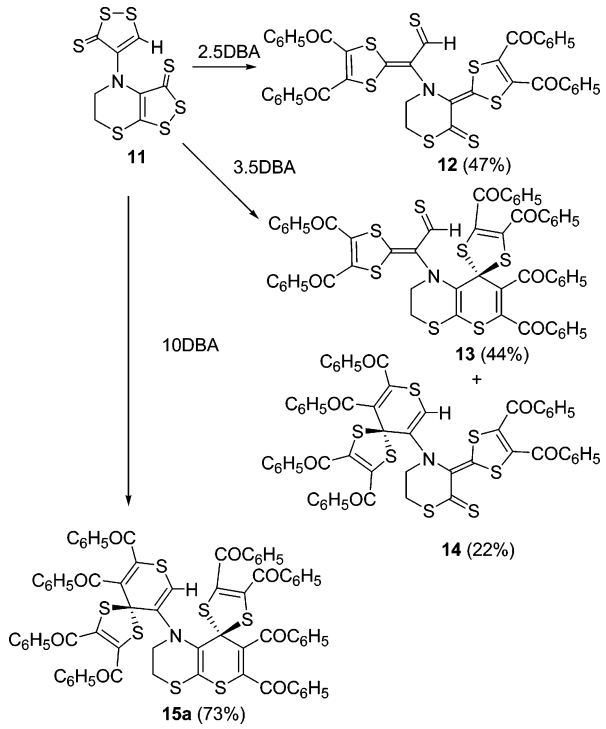
SCHEME 5



The facile 1:4 cycloaddition of bisdithiolothiazine dithiones and DBA was proved by performing the reaction of the *N*-stearyl- and *N*-laurylbis[1,2]dithiolo[1,4]-thiazines **4c**,**d**[18] (1 equiv) with DBA (10−15 equiv) in refluxing benzene for 2.5 h, that gave the corresponding 1:4 adducts **10c** (yellow solid, mp 76−77 °C, 62%) and **10d** (yellow solid, mp 65−66 °C, 96%), whose structures were elucidated by spectroscopy and microanalysis (Scheme 5).

In our hands, the cycloaddition of polycyclic condensed 1,2-dithiolethiones was strongly dependent on the reactivity of the dipolarophile and the reaction conditions, but a careful control of the latter permitted achievement of selectivity in most of the examples studied. We applied this knowledge to the cycloaddition of the bisdithiolo[1,4]-thiazine **11**[9b] that contained two different dithiolethione groups with the same dipolarophiles, on the way to new branched heterocycles. Treatment of **11** (1 equiv) with an excess of DMAD (5 equiv) in refluxing benzene for 15 min gave three new spots on TLC as the spot of **11** progressively faded, but the expected products decomposed during workup and could not be isolated. Similar results were obtained by using di-*tert*-butyl acetylenedicarboxylate in place of DMAD under similar conditions. Instead, the reaction of **11** (1 equiv) and DBA (2.5 equiv) in benzene at room temperature for 20 min gave only a new product **12** as a brown solid (mp 118−119 °C, 47%), which was sufficiently stable to be purified by column chromatography and characterized by spectroscopy (Scheme 6). MS (FAB$^+$) of **12** showed a molecular peak corresponding to the addition of two molecules of DBA. The ^{1}H NMR spectrum showed a singlet at around δ 11, and the ^{13}C NMR spectrum showed a signal at around δ 200, assigned to a tertiary CH group from DEPT experiments, all indicating the presence of a rare thioaldehyde function in **12**. Two multiplets by δ 7 in ^{1}H NMR, confirmed by the presence of characteristic aromatic signals in ^{13}C NMR, indicated the presence of four phenyl rings, four multiplets at δ 3−4 corresponded to the four

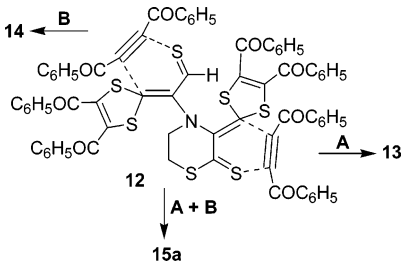
SCHEME 6



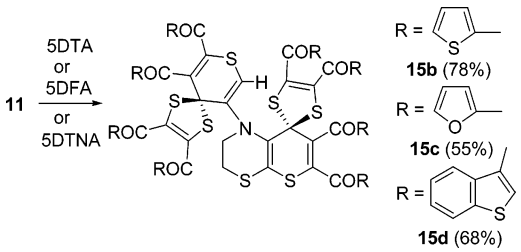
protons in the dihydrothiazine ring, and the presence of a thione and three carbonyl groups was seen in the ^{13}C NMR spectrum and confirmed by IR. With these data, we assigned to **12** the structure of the 1:2 adduct shown in Scheme 6, that contained two different heterodiene groups, each one a possible substrate of further cycloadditions. Compound **12** steadily decomposed at room temperature under air, but it could be stored for several months under inert atmosphere at −18 °C.

To check the stepwise cycloaddition of dipolarophiles, we performed the reaction of **11** (1 equiv) and DBA (3.5 equiv) in benzene at room temperature for 45 min, from which we obtained, after chromatography, a mixture of **13** (brown solid, mp 109−110 °C, 44%) and the more polar **14** (red solid, mp 116−117 °C 22%) (Scheme 6). Products **13** and **14** showed identical molecular mass peaks in EM (FAB$^+$) that corresponded to isomeric 1:3 adducts, confirmed by microanalyses. The ^{1}H NMR spectrum of compound **13** showed a singlet at around δ 11, and its ^{13}C NMR spectrum showed a signal at around δ 200 (a tertiary CH from DEPT experiments), indicating a thioaldehyde function in **13**, confirmed by IR. On the contrary, the ^{1}H NMR spectrum of **14** did not show a thioaldehyde function, but showed instead a vinylic proton signal at around δ 6.5, and the ^{13}C NMR spectrum showed a thione group at δ 197, confirmed by IR. Six phenyl rings, four cyclic protons, and five carbonyl group signals were found in the ^{1}H and ^{13}C NMR spectra of both **13** and **14**; therefore, we assigned the thioaldehyde structure **13** to the main product and the thiolactone structure **14** to the minor product. Thioaldehyde **13** came from a hetero-Diels−Alder cycloaddition of DBA to the α,β-unsaturated thiolactone present in **12** (path **A** in Scheme 7), but thiolactone **14** was formed by cycloaddition to the α,β-unsaturated thioaldehyde in **12** (path **B** in Scheme 7). Although thioaldehydes are considered

SCHEME 7



SCHEME 8



good substrates for cycloadditions, the reactivity of the heterodiene containing it was just one-half of that shown by the heterodiene containing the thiolactone group. Thioaldehyde **13** steadily decomposed under air and moisture, but it could be stored indefinitely under inert atmosphere; thioketone **14** was stable in normal conditions.

Both **13** and **14** still contained a heterodiene system, although an additional hetero-Diels−Alder reaction would give the same product from both compounds (path **A** + **B** in Scheme 7). Consequently, the reaction of **11** (1 equiv) with an excess of DBA (10 equiv) in refluxing benzene for 1 h gave, after chromatography, a unique product **15a** as a yellow solid of mp 209−210 °C (73%), which was stable at room temperature (Scheme 6). MS (FAB^+) and microanalysis of **15a** gave a molecular formula $C_{72}H_{45}NO_8S_7$; its ^{13}C NMR spectrum showed six carbonyl groups, five sp^2-tertiary carbon signals, 14 CH aromatic signals, two sp^3-quaternary carbons, and two methylene groups, and its ^1H NMR spectrum showed signals corresponding to 40 aromatic protons, a vinylic proton, and four aliphatic protons. From all of these data, we assigned the bis-spiranic structure **15a**, a new highly branched molecule with a complex heterocyclic core.

We expanded these syntheses by cycloaddition of the dithiolothiazine dithione **11** and DBA analogues. Thus, reaction of **11** (1 equiv) and di(2-thienoyl)acetylene[19] (DTA, 5 equiv) in refluxing toluene for 1 h gave the corresponding 1:4 adduct **15b** (orange solid, mp 159−160 °C, 78%), which was elucidated by spectroscopy and microanalysis (Scheme 5). Analogously, reaction of **11** (1 equiv) and di(2-furoyl)acetylene (DFA, 5 equiv) under the same conditions gave **15c** (dark yellow solid, mp 169−170 °C, 55%), and a similar reaction with di(3-thianaphthenecarbonyl)acetylene (DTNA, 4.5 equiv) gave **15d** (dark yellow solid, mp 180−181 °C, 68%) whose structures were elucidated by spectroscopy and microanalyses (Scheme 8).

(19) Skabara, P. J.; Serebryakov, I. M.; Roberts, D. M.; Perepichka, I. F.; Coles, S. J.; Hursthouse, M. B. *J. Org. Chem.* **1999**, *64*, 6418−6424.

TABLE 1. Peak Potentials for Cyclic Voltammograms Registered at 100 mV/s

compound	E_p^{ox} (V)	E_p^{red} (V)
5a	1.38	−1.09
5b	1.43	−0.98
8a	1.42	−1.01
10a	1.45	−1.10
15b	1.34	−1.05
15c	1.32	−1.08
15d	1.34	−1.07

We performed cyclic voltammetry experiments of 5×10^{-4} M solutions of **5a**,**b** and **8a**, having an extended conjugation, and of tetra-adducts **10a** and **15b**−**d** in dichloromethane at 20 °C, using Bu_4NPF_6 as supporting electrolyte in an approximate 0.1 M concentration, a platinum ball as a working electrode, platinum wire as an auxiliary electrode, and saturated calomelanes as a reference electrode. The cyclic voltammograms were registered at different scanning velocities, showing irreversible processes for all of the compounds tested. The comparison between the intensities of the first oxidation and first reduction waves showed, in all cases, electronic transfers in which twice as many electrons were apparently involved in the reduction than in the oxidation processes, although controlled potential electrolysis was not used to accurately determine the number of implied electrons. All adducts underwent similar redox processes, regardless of being di- or tetra-adducts, and independently of the substituents on the nitrogen and on the 1,3-dithiole rings. Table 1 summarizes the values of the reduction and oxidation processes for **5a**,**b**, **8a**, **10a**, and **15b**−**d**, measured under analogous conditions.

Conformational Studies

The presence of conformers of **6a** and **9a** that came from restricted inversion of nitrogen, as seen in their ^1H NMR spectra, was not further studied because the coalescence of signals should happen to high temperatures not available experimentally. Yet the tetra-adduct **10a** showed a broad methylene signal at room temperature, so we carried out dynamic NMR studies by recording ^1H NMR spectra between −80 and 40 °C (Figure 2). The methylene signal was completely resolved as a quartet at 313 K (40 °C); the coalescence temperature was 247 K. As the temperature was further lowered, the broad singlet decreased its intensity until apparently disappearing at 243 K, and reappearing first at 233 K as two new separated singlets, one of which split into two at 213 K. The use of the Eyring equation[20] for the given value of the coalescence temperature resulted in a calculated rotation barrier of 11.0 kcal/mol.

We expected that tetra-adduct **10a** had a symmetric structure, but from the dynamic NMR experiments it was obvious that **10a** should exist as two diastereomeric structures that interconvert through a barrier of about 11 kcal/mol. Modelization by PM3 methods showed that the parent heterocyclic core of **10a** existed as two

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

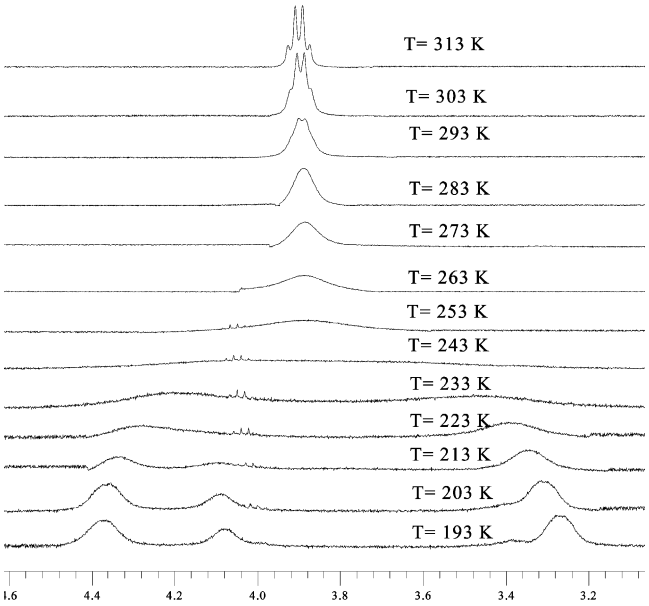


FIGURE 2. ^{1}H NMR spectra of adduct **10a** registered between −80 and 40 °C.

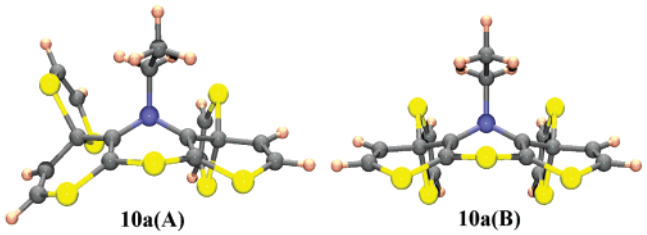


FIGURE 3. The two energetically equivalent conformers of the parent system of **10a**.

energetically equivalent conformers asymmetrically and symmetrically folded (Figure 3).

Yet the addition of the eight benzoyl groups to models **10a**(**A**) and **10a**(**B**) afforded local minima of different energies; the asymmetrically folded structure **10a**(**C**) was more stable than the symmetrically folded one **10**(**D**) by 4 kcal/mol (Figure 4), so it is expected that **10a**(**C**) will be more abundant than **10a**(**D**) and the dynamic NMR signals should correspond to the slow nitrogen inversion of **10a**(**C**).

Another important feature was seen in the ^{1}H NMR spectrum of **15a**−**d**. One aliphatic proton of **15a**, and similarly for **15b**−**d**, appeared at δ 5.3, and the rest appeared within δ 3.6−3.3 (Figure 5). This unusual chemical shift cannot be due to chemical bonding, which is comparable for all four protons of the two methylene groups, but it should come from the sterically congested environment near the nitrogen atom. To test this hypothesis, we studied this structure by molecular modeling. We obtained a few minimized structures having comparable energies, the only difference being the relative dispositions of benzoyl groups in each double bond. The lowest energy structure showed a proton in an α-position of the nitrogen that was situated at 2.7 Å of a 1,3-dithiole group (Figure 6). All of the other related structures had the same feature.

In all cases we have studied, the initial geometries for PM3 optimization were obtained by using MM2 minimization methods and systematic variation of dihedral angles of heterocycles and peripheral groups, all with HyperChem 5.11.[21]

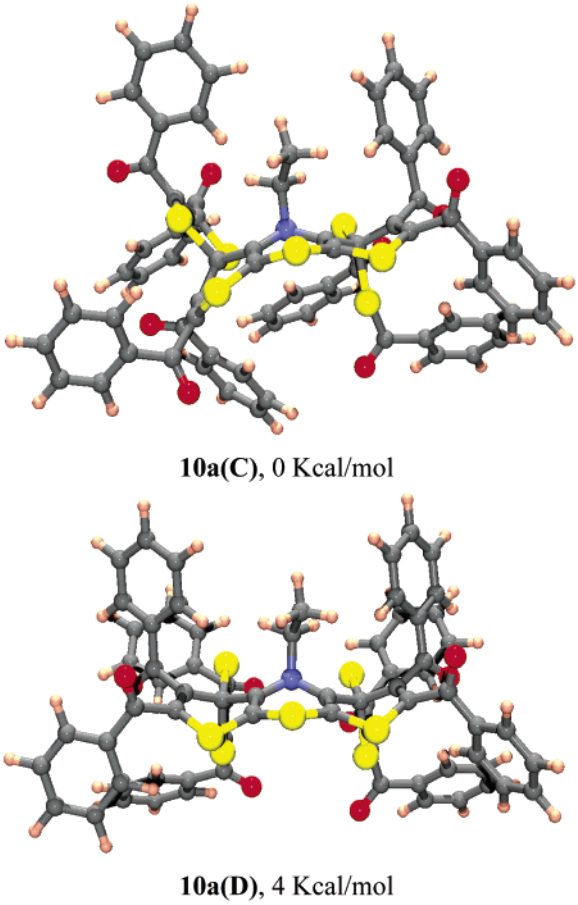


FIGURE 4. The two energetically nonequivalent minimum conformers of **10a**.

Conclusions

We have shown that cascade cycloadditions of polycyclic bis-1,2-dithiole-3-thiones to activated acetylenes constitute a practical method for the tailored synthesis of fully substituted mono- and bisdithiafulvenyl-1,4-thiazines and mono- and bis-spiro-1,3-dithiolethiopyranes fused to 1,4-thiazines and pyrroles. Some of these polysulfur heterocycles contained long hydrocarbon chains, amphiphilic molecules potentially useful in the construction of self-assembled molecular vesicles for easy encapsulation. The reported method has proved to be very flexible, as reaction conditions can be carefully controlled to obtain selectively the 1:2, 1:3, or 1:4 cycloadducts in most cases studied. In addition, two obtained products contained a thioaldehyde group, a very reactive function. Taking into account that all starting heterocycles were obtained in one-pot reactions from tertiary amines, this method permitted the preparation of highly branched polysulfur−nitrogen heterocycles in only two steps from tertiary amines, S_2Cl_2, and bis-activated alkynes.

(21) HyperChem 5.11 (Hypercube, Inc.).

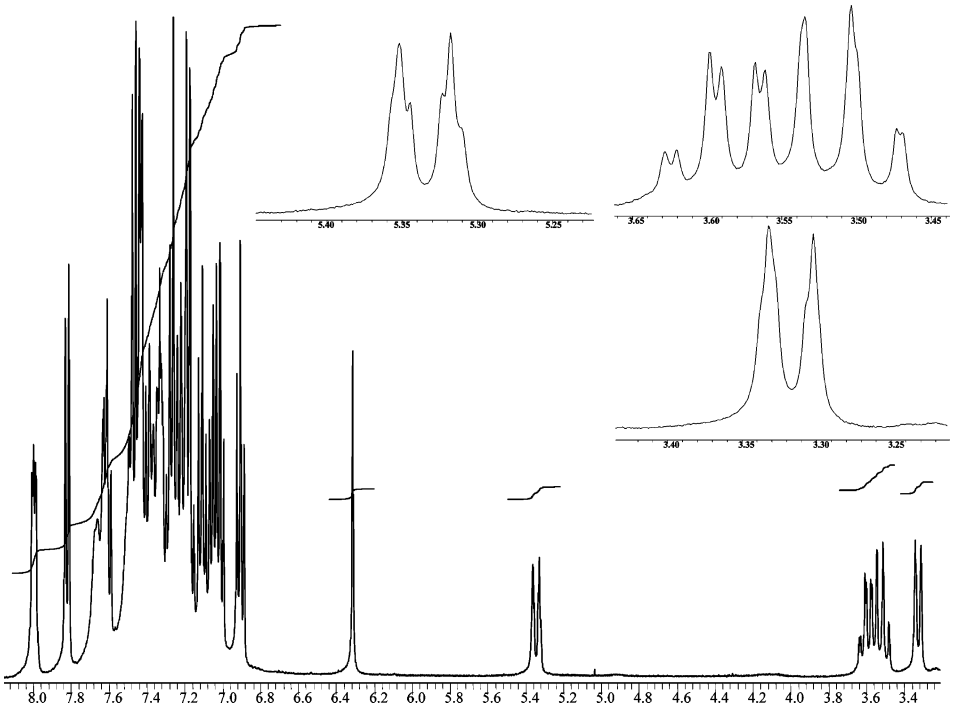


FIGURE 5. ^{1}H NMR spectrum of adduct **15a** and amplifications of the aliphatic region.

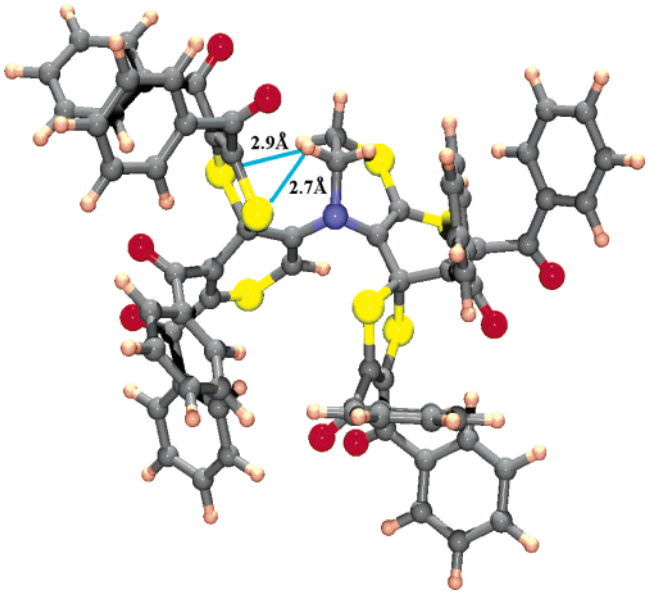


FIGURE 6. The lowest energy conformer of adduct **15a** showing the main interactions.

Experimental Section

Bis[1,2]dithiolopyrrole dithione **1**,[7b] bis[1,2]dithiolo[1,4]-thiazine dithiones **4a**−**d**,[7b,9b,18] and [1,2]dithiolo[1,4]thiazine dithione **11**[9b] were prepared as described. Dibenzoylacetylene[14] (DBA) and di(2-thienoyl)acetylene[19] (DTA) were prepared following known methods. Acyl chlorides, diisopropylamine, disulfur dichloride, and dimethyl- (DMAD) or di-*tert*-butyl acetylenedicarboxylate were purchased and used without further purification. CH_2 and CH groups were identified by DEPT experiments on representative examples. General experimental methods can be found in previous papers.[12]

Reaction of Bis[1,2]dithiolopyrrole 1 and DMAD. DMAD (231 mg, 200 μL, 1.627 mmol) was added to a solution of bis-[1,2]dithiolopyrrole **1** (100 mg, 0.326 mmol) in toluene (15 mL). The resulting solution was stirred under reflux for 3 h, the solvent was removed in the rotary evaporator, and the resulting solid was purified by MPLC (petroleum ether to CH_2Cl_2–ethyl acetate 17:3) to give **2a** as a yellow solid (CH_2Cl_2–petroleum ether) (220 mg, 0.25 mmol, 77%) and **3a** as a mauve solid (CH_2Cl_2−petroleum ether) (22 mg, 0.026 mmol, 8%).

Octamethyl 4,6-Bis{spiro(1,3-dithiol-2-yl)}-5-ethylbisthiopyrano[2,3-*b*:2′,3′-*d*]pyrrole-2,3,4′,4″,5′,5″,7,8-octacarboxylate 2a. mp 224−226 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.22 (q, J = 8.0 Hz, 2H, CH_2), 3.91 (s, 6H, 2 × CH_3), 3.87 (s, 6H, 2 × CH_3), 3.82 (s, 12H, 4 × CH_3), 1.85 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.3, 162.8, and 160.3 (3 × *C*═O), 131.0, 127.5, 125.2, 122.8, and 108.1 (5 × sp^2 *tertiary* C), 64.7 (*quaternary* C), 53.8, 53.2, and 53.2 (3 × *C*H_3, DEPT), 43.3 (*C*H_2, DEPT), 16.6 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 1730 (C═O), 1572, 1433, 1256, 1042, 783; MS (FAB+) *m*/*z* 876 (M + 1, 100), 844 (10), 816 (20), 702 (5), 670 (5), 495 (5). Anal. Calcd for $C_{32}H_{29}NO_{16}S_6$: C, 43.88; H, 3.34; N, 1.60. Found: C, 43.62; H, 3.31; N, 1.49.

Octamethyl 4,6-Bis{spiro(1,3-dithiol-2-yl)}-5-ethylthiopyrano[2,3-*b*]cyclopenta[*d*]pyrrole-2,3,4′,4″,5′,5″,7,8-octacarboxylate 3a. mp 221−222 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.95 (q, J = 7.0 Hz, 2H, CH_2), 4.00 (s, 6H, 2 × CH_3), 3.93 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 3.83 (s, 6H, 2 × CH_3), 0.99 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.5, 165.1, 163.7, 162.5, 162.0, and 160.2 (6 × *C*═O), 143.6, 139.0, 133.1, 132.9, 127.6, 125.1, 124.5, 116.7, 114.5, and 112.4 (10 × sp^2 *tertiary* C), 64.5 (*quaternary* C), 54.1, 53.4, 52.7, 52.2, and 52.1 (5 × *C*H_3), 45.8 (*C*H_2), 14.4 (*C*H_3); IR (KBr, cm^{-1}) ν 1748 (C═O), 1572, 1435, 1242, 1026. Anal. Calcd for $C_{32}H_{29}NO_{16}S_5 \cdot {}^1/_2CH_2Cl_2$: C, 44.04; H, 3.41; N, 1.58. Found: C, 44.40; H, 3.29; N, 1.50.

2,3,7,8-Tetrabenzoyl-4,6-bis{spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)}-5-ethylbisthiopyrano[2,3-*b*:2′,3′-*d*]pyrrole 2b. DBA (381 mg, 1.627 mmol) was added to a solution of bis[1,2]-dithiolopyrrole **1** (100 mg, 0.326 mmol) in benzene (15 mL). The resulting solution was stirred under reflux for 15 min, the solvent was removed in the rotary evaporator, and the resulting solid was purified by MPLC (petroleum ether to CH_2Cl_2) to give **2b** as a yellow solid (CH_2Cl_2–petroleum ether)

(182 mg, 0.15 mmol, 45%), mp 140−142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80−7.20 (m, 40H, 8 × C_6H_5), 5.69 (q, J = 6.7 Hz, 2H, CH_2), 2.10 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.3, 191.3, and 186.8 (3 × *C*═O), 138.4, 137.3, 136.8, and 135.2 (4 × sp^2 *tertiary* C), 134.6, 133.8, and 133.3 (3 × *C*H aromatic, DEPT), 132.9, 131.9 (2 × sp^2 *tertiary* C), 130.5, 130.3, 128.9, 128.5, and 128.4 (5 × *C*H aromatic, DEPT), 123.6 and 108.8 (2 × sp^2 *tertiary* C), 64.2 (*quaternary* C), 43.9 (*C*H_2, DEPT), 17.1 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 3059, 1662 (C═O), 1595, 1531, 1448, 1255, 817, 689; MS (FAB+) *m*/*z* 1243 (M^+, 15), 1138 (1), 978 (2), 681 (1), 105 ($PhCO^+$, 65). Anal. Calcd for $C_{72}H_{45}NO_8S_6$: C, 69.49; H, 3.64; N, 1.13. Found: C, 69.62; H, 3.78; N, 1.12.

Tetramethyl 4-Ethyl-3,5-bis(1,3-dithiol-2-ylidenyl)-2,6-dithioxo[1,4]thiazine-4′,4″,5′,5″-tetracarboxylate 5a. Thermal Procedure: DMAD (58 mg, 50 μL, 0.408 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4a** (55 mg, 0.162 mmol) in benzene (5 mL), and the resulting solution was stirred under reflux for 10 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether to CH_2Cl_2) to give **5a** as an orange solid (CH_2Cl_2–petroleum ether) (45 mg, 0.072 mmol, 44%), mp 119−120 °C. **Catalyzed Procedure:** DMAD (26 mg, 23 mL, 0.184 mmol) was added to a solution of **4a** (25 mg, 0.074 mmol) and $Sc(OTf)_3$ (9 mg, 0.018 mmol) in dichloromethane (2 mL), and the resulting solution was stirred at room temperature for 2 h and worked-up as previously. Flash chromatography (CH_2Cl_2−petroleum ether 1:1 to CH_2Cl_2) of the reaction residue gave **5a** (41 mg, 0.066 mmol, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.98 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 3.38 (q, J = 7.2 Hz, 2H, CH_2), 1.27 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.6 (*C*═S), 160.9 (sp^2 *tertiary* C), 159.9 and 159.6 (2 × *C*═O), 133.7, 133.1, and 132.8 (3 × sp^2 *tertiary* C), 54.0 and 53.8 (2 × *C*H_3), 49.8 (*C*H_2), and 13.6 (*C*H_3); IR (KBr, cm^{-1}) ν 1754 (C═O), 1731 (C═O), 1576, 1437, 1235 (C═S), 1002, 966, 684; MS (FAB+) *m*/*z* 624 (M + 1, 45), 594 (M − 29, 30), 562 (10), 533 (6), 91 (50), 77 (55), 69 (75), 55 (100). Anal. Calcd for $C_{20}H_{27}NO_8S_7$: C, 38.51; H, 2.75; N, 2.25. Found: C, 38.52; H, 2.78; N, 2.16.

Hexamethyl 2-Thioxo-3-(1,3-dithiol-2-ylidenyl)-4-ethyl-5-spiro(1,3-dithiol-2-yl)thiopyrano[2 ,3-*e*][1,4]thiazine-4′,4″,5′,5″,6,7-hexacarboxylate 6a. DMAD (84 mg, 73 μL, 0.592 mmol) was added to a solution of bis[1,2]dithiolo[1,4]-thiazine **4a** (40 mg, 0.118 mmol) in benzene (5 mL), and the resulting solution was stirred under reflux for 15 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether to CH_2Cl_2−ethyl acetate 9:1) to give **6a** as an orange solid (CH_2Cl_2−ethyl acetate) (43 mg, 0.056 mmol, 48%), mp 87−88 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.95 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 3.84 (s, 6H, 2 × CH_3), 3.73 (s, 3H, CH_3), 3.64 (six signals, double quartet, J = 14.2 Hz, J = 7.1 Hz, 1H, $^1/_2CH_2$), 3.18 (six signals, double quartet, J = 14.2 Hz, J = 7.1 Hz, 1H, $^1/_2CH_2$), and 1.19 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.6 (*C*═S), 165.1, 164.8, 161.3, 160.4, 160.1, and 159.5 (6 × *C*═O), 137.3, 134.9, 132.2, 131.8, 128.7, 128.3, 127.2, 126.8, 124.7, 115.5 (10 × sp^2 *tertiary* C), 71.4 (*quaternary* C), 53.8, 53.7, 53.2, and 53.1 (4 × *C*H_3, DEPT), 50.0 (*C*H_2, DEPT), and 12.9 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 1735 (C═O), 1580, 1432, 1250 (C═S); MS (FAB+) *m*/*z* 766 (M + 1, 5), 577 (3), 459 (2), 327 (6), 221 (5), 207 (7). Anal. Calcd for $C_{26}H_{23}NO_{12}S_7$: C, 40.77; H, 3.03; N, 1.83. Found: C, 40.84; H, 3.14; N, 1.84.

Octamethyl4,6-Bis{spiro(1,3-dithiol-2-yl)}-5-ethylbisthiopyrano[2,3-*b*:2′,3′-*e*][1,4]thiazine-2,3,4′,5′,4″,5″,7,8-octacarboxylate 7a. DMAD (251 mg, 218 μL, 1.770 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4a** (20 mg, 0.059 mmol) in toluene (5 mL), and the resulting solution was stirred under reflux for 90 min. Five new portions of DMAD (251 mg, 218 μL, 1.770 mmol) were then added successively at intervals of 90 min, while the reflux was maintained. After the last addition of DMAD, the reflux was maintained for a further 90 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (CH_2Cl_2 to CH_2Cl_2−ethyl acetate 9:1) to give **7a** as a yellow solid (CH_2Cl_2−ethyl acetate) (45 mg, 0.050 mmol, 85%), mp 58−59 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.90 (s, 6H, 2 × CH_3), 3.83 (s, 6H, 2 × CH_3), 3.77 (s, 6H, 2 × CH_3), 3.68 (s, 6H, 2 × CH_3), 3.27 (q, J = 7.2 Hz, 2H, CH_2), and 1.14 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.8, 161.2, 160.2, and 160.1 (4 × *C*═O), 140.2, 131.2, 128.6, 128.2, 127.8, and 125.1 (6 × sp^2 *tertiary* C), 71.5 (*quaternary* C), 53.7, 53.1, 52.9, and 52.8 (4 × *C*H_3), 50.0 (*C*H_2), 13.3 (*C*H_3); IR (KBr, cm^{-1}) ν 1736 (C═O), 1582, 1435, 1259; MS (FAB+) *m*/*z* 908 (M + 1, 19), 878 (M − 29, 2), 848 (M − 59, 5), 734 (3). Anal. Calcd for $C_{32}H_{29}NO_{16}S_7 \cdot CH_2Cl_2$: C, 39.92; H, 3.15; N, 1.41. Found: C, 40.31; H, 3.03; N, 1.17.

Tetramethyl 4-(2-Chloroethyl)-3,5-bis(1,3-dithiol-2-ylidenyl)-2,6-dithioxo[1,4]thiazine-4′,4″, 5′,5″-tetracarboxylate 5b. DMAD (58 mg, 50 μL, 0.408 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4b** (60 mg, 0.161 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 45 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 1:1 to CH_2Cl_2) to give **5b** as a red solid (CH_2Cl_2−petroleum ether) (72 mg, 0.110 mmol, 68%), mp 178−179 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.96 (s, 6H, 2 × CH_3), 3.91 (s, 3H, 2 × CH_3), 3.72 (double triplet, J = 7.2 Hz, J = 2.5 Hz, 2H, CH_2), 3.58 (double triplet, J = 7.2 Hz, J = 2.5 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 195.4 (*C*═S), 160.8 (sp^2 *tertiary* C), 159.6 and 159.5 (2 × *C*═O), 133.5, 133.1, and 132.2 (3 × sp^2 *tertiary* C), 55.9 (*C*H_2, DEPT), 54.0 and 53.8 (2 × *C*H_3, DEPT), 40.8 (*C*H_2, DEPT); IR (KBr, cm^{-1}) ν 1732 (C═O), 1712 (C═O), 1574, 1453, 1428, 1448, 1268 (C═S), 1019, 978; MS (FAB+) *m*/*z* 658 (M + 1, 5), 626 (M − 31, 1), 594 (M − 63, 6), 563 (2), 399 (3) 147 (25), 91 (45), 81 (32), 73 (100), 55 (60). Anal. Calcd for $C_{20}H_{16}ClNO_8S_7$: C, 36.50; H, 2.45; N, 2.13. Found: C, 36.51; H, 2.38; N, 1.95.

Tetramethyl 4-Stearyl-3,5-bis(1,3-dithiol-2-ylidenyl)-2,6-dithioxo[1,4]thiazine-4′,4″,5′,5″-tetracarboxylate 5c. DMAD (58 mg, 50 μL, 0.408 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4c** (91 mg, 0.162 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 20 min. The solvent was then removed in the rotary evaporator, and the resulting residue was purified by flash chromatography (petroleum ether−CH_2Cl_2 3:2) to give **5c** as a red oily solid (82 mg, 0.097 mmol, 60%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.98 (s, 6H, 2 × CH_3), 3.93 (s, 6H, 2 × CH_3), 3.25 (m, 2H, CH_2), 1.66 (m, 2H, CH_2), 1.24 (m, 30H, 15 × CH_2), 0.87 (t, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 195.6 (*C*═S), 160.5 (sp^2 *tertiary* C), 159.8 and 159.6 (2 × *C*═O), 133.6, 133.5, and 132.8 (3 × sp^2 *tertiary* C), 55.4 (*C*H_2), 53.9 and 53.7 (2 × *C*H_3), 31.9, 29.7, 29.6, 29.5, 29.3, 28.2, 27.3, and 22.7 (8 × *C*H_2), 14.1 (*C*H_3); IR (KBr, cm^{-1}) ν 2956, 2924, 2852, 1736 (C═O), 1729 (C═O), 1260 (C═S); MS (FAB+) *m*/*z* 848 (M + 1, 4), 816 (1), 594 (5), 562 (3), 275 (4), 69 (62), 55 (85). Anal. Calcd for $C_{36}H_{49}NO_8S_7$: C, 50.97; H, 5.82; N, 1.65. Found: C, 51.37; H, 5.79; N, 1.70.

4-Ethyl-3,5-bis(4,5-dibenzoyl-1,3-dithiol-2-ylidenyl)-[1,4]thiazine-2,6-dithione 8a. DBA (95 mg, 0.408 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4a** (55 mg, 0.162 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 5 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 2:3) to give **8a** as an orange solid (CH_2Cl_2−petroleum ether) (88 mg, 0.109 mmol, 67%), mp 115−116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (m, 12H, 12 × aromatic CH), 7.25 (m, 8H, 8 × aromatic CH), 3.48 (q, J = 7.2 Hz, 2H, CH_2), 1.36 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.4 (*C*═S), 186.8 and 186.6 (2 × *C*═O), 161.5, 140.6, 140.3, 136.6, and 136.5 (5 × sp^2 *tertiary* C and *C* aromatic), 134.1 and 134.0 (2 × *C*H aromatic), 133.0 (sp^2 *tertiary* C), 129.0, 128.9, and 128.7 (3 ×

*C*H aromatic), 49.8 (*C*H_2), 13.8 (*C*H_3); IR (KBr, cm^{-1}) ν 1650 (C═O), 1595, 1436, 1261 (C═S), 974, 693; MS (FAB+) *m/z* 808 ($M^+ + 1$, 5), 778 (M − 29, 5), 776 (1), 371 (13), 231 (64), 154 (96), 137 (100), 109 (27). Anal. Calcd for $C_{40}H_{25}NO_4S_7$: C, 59.45; H, 3.12; N, 1.73. Found: C, 59.54; H, 3.20; N, 1.58.

Reaction of Bis[1,2]dithiolo[1,4]thiazine 4a and 5 equiv of DBA. DBA (138 mg, 0.592 mmmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4a** (40 mg, 0.118 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 15 min, as the reaction was monitored by TLC. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 2:3 to CH_2Cl_2) to give **9a** as an orange solid (CH_2Cl_2−petroleum ether) (33 mg, 0.032 mmol, 27%) and **10a** as a yellow solid (CH_2Cl_2−petroleum ether) (83 mg, 0.065 mmol, 55%).

3-(4,5-Dibenzoyl-1,3-dithiol-2-ylidenyl)-4-ethyl-5-spiro-(4,5-dibenzoyl-1,3-dithiol-2-yl)-6,7-dibenzoylthiopyrano-[2,3-*b*][1,4]thiazine-6-thione 9a. mp 115−116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J = 7.4 Hz, 2H, 2 × aromatic C*H*), 7.72 (d, J = 7.4 Hz, 2H, 2 × aromatic C*H*), 7.62−7.06 (m, 26H, 26 × aromatic C*H*), 3.76 (six signals, double quartet, J = 14.2 Hz, J = 7.1 Hz, 1H, $^1/_2CH_2$), 3.40 (six signals, double quartet, J = 14.2 Hz, J = 7.1 Hz, 1H, $^1/_2CH_2$), 1.36 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4 (*C*═S), 193.0, 189.8, 187.0, 186.8, 186.6, and 186.3 (6 × *C*═O), 164.0, 142.1, 141.1, 140.2, 138.0, 137.2, 137.1, 137.0, 136.6, 136.5, 136.1, 135.1, 134.5, 134.1, 134.0, 133.9, 133.2, 133.1, 131.7, 131.3, 129.8, 129.4, 129.0, 128.9, 128.8, 128.6, 128.3, 128.2, and 127.5 (29 × sp^2 *tertiary* C, *C*H aromatic, and *C* aromatic), 71.1 (*quaternary* C), 50.5 (*C*H_2,), and 13.1 (*C*H_3,); IR (KBr, cm^{-1}) ν 2924, 1661 (C═O), 1595, 1538, 1448, 1260 (C═S), 691; MS (FAB+) *m/z* 1042 (M + 1, 1), 744 (1), 550 (60), 522 (40), 105 ($PhCO^+$, 35), 81 (40), 69 (75), 55 (100). Anal. Calcd for $C_{56}H_{35}NO_6S_7$: C, 64.53; H, 3.38; N, 1.34. Found: C, 64.64; H, 3.31; N, 1.25.

2,3,7,8-Tetrabenzoyl-4,6-bis{spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)}-5-ethylbisthiopyrano[2,3-*b*:2′,3′-*e*][1,4]-thiazine 10a. Independent Synthesis: DBA (206 mg, 0.880 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4a** (50 mg, 0.147 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 60 min. Three new portions of DBA (69 mg, 0.295 mmol) were then added successively at intervals of 30 min, while the reflux was maintained. After the last addition of DBA, the reflux was maintained for a further 30 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 1:1 to CH_2Cl_2−ethyl acetate 98:2) to give **10a** as a yellow solid (CH_2Cl_2−petroleum ether) (177 mg, 0.139 mmol, 95%), mp 135−136 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J = 7.2 Hz, 4H, 4 × aromatic C*H*), 7.82 (d, J = 7.2 Hz, 4H, 4 × aromatic C*H*), 7.62 (t, J = 7.4 Hz, 2H, 2 × aromatic C*H*), 7.39 (m, 24H, 24 × aromatic C*H*), 7.07 (q, J = 7.2 Hz, 6H, 6 × aromatic C*H*), 3.88 (broad singlet, 2H, CH_2), 1.49 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.1, 189.8, 187.2, and 186.7 (4 × *C*═O), 143.4, 137.3, 137.1, 137.0, 135.2 (5 × sp^2 *tertiary* C and *C* aromatic), 134.5, 134.0, 133.0, 132.9 (4 × *C*H aromatic, DEPT), 132.6 (sp^2 *tertiary* C), 129.8, 129.7, 128.8, 128.7, and 128.2 (5 × *C*H aromatic, DEPT), 71.2 (*quaternary* C), 52.6 (*C*H_2, DEPT), 13.2 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 3060, 2925, 1665 (C═O), 1595, 1578, 1536, 1448, 1258, 691; MS (FAB+) *m/z* 1275 (M^+, 1), 1170 (1), 977 (1), 884 (1), 732 (1), 670 (1), 550 (6), 522 (4), 105 ($PhCO^+$, 42). Anal. Calcd for $C_{72}H_{45}NO_8S_7$: C, 67.74; H, 3.55; N, 1.10. Found: C, 67.67; H, 3.18; N, 1.30.

2,3,7,8-Tetrabenzoyl-4,6-bis{spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)}-5-stearylbisthiopyrano[2,3-*b*:2′,3′-*e*][1,4]-thiazine 10c. DBA (206 mg, 0.880 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4c** (83 mg, 0.147 mmol) in benzene (15 mL), and the resulting solution was stirred under reflux for 60 min. Three new portions of DBA (103 mg, 0.441 mmol) were then added successively at intervals of 30 min, while the reflux was maintained. After the last addition of DBA, the reflux was maintained for an additional 30 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 1:1 to CH_2Cl_2−ethyl acetate 95:5) to give **10c** as a yellow solid (CH_2Cl_2−petroleum ether) (137 mg, 0.091 mmol, 62%), mp 76−77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 7.2 Hz, 4H, 4 × aromatic C*H*), 7.82 (d, J = 7.2 Hz, 4H, 4 × aromatic C*H*), 7.63 (t, J = 7.5 Hz, 2H, 2 × aromatic C*H*), 7.40 (m, 24H, 24 × aromatic C*H*), 7.06 (q, J = 7.9 Hz, 6H, 6 × aromatic C*H*), 3.80 (broad singlet, 2H, CH_2), 1.97 (unresolved quintet, 2H, CH_2), 1.36 (m, 2H, CH_2), 1,26 (m, 28H, 14 × CH_2), 0.88 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.2, 189.9, 187.2, and 186.7 (4 × *C*═O), 143.1, 137.4, 137.3, 137.2, 137.1, 135.3, 134.6, 134.0, 133.4, 133.0, 132.9, 132.5, 129.9, 129.6, 128.8, 128.7, 128.4, 128.3, and 126.9 (19 × sp^2 *tertiary* C, *C*H aromatic, and *C* aromatic), 71.0 (*quaternary* C), 32.3, 31.9, 29.8, 29.7, 29.6, 29.3, 28.0, 27.4, 22.9, and 22.7 (10 × *C*H_2, DEPT), 14.1 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 2923, 2852, 1664 (C═O), 1596, 1578, 1536, 1448, 1314, 1258, 691; MS (FAB+) *m/z* 1500 (M + 1, 100), 1396 (30), 1202 (78), 1096 (20), 904 (22), 545 (45), 439 (72). Anal. Calcd for $C_{88}H_{77}NO_8S_7$: C, 70.42; H, 5.17; N, 0.93. Found: C, 70.66; H, 5.16; N, 0.80.

2,3,7,8-Tetrabenzoyl-4,6-bis{spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)}-5-laurylbisthiopyrano[2,3-*b*:2′,3′-*e*][1,4]-thiazine 10d. DBA (206 mg, 0.880 mmol) was added to a solution of bis[1,2]dithiolo[1,4]thiazine **4d** (70 mg, 0.146 mmol) in benzene (15 mL), and the resulting solution was stirred under reflux for 60 min. A new portion of DBA (138 mg, 0.590 mmol) was added while the reflux was maintained, and the mixture was heated under reflux for an additional 30 min. The solvent was then removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 1:1 to CH_2Cl_2) to give **10d** as a yellow solid (CH_2Cl_2−petroleum ether) (200 mg, 0.141 mmol, 96%), mp 65−66 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 7.1 Hz, 4H, 4 × aromatic C*H*), 7.81 (d, J = 7.1 Hz, 4H, 4 × aromatic C*H*), 7.62 (t, J = 7.5 Hz, 2H, 2 × aromatic C*H*), 7.41 (m, 24H, 24 × aromatic C*H*), 7.06 (q, J = 7.6 Hz, 6H, 6 × aromatic C*H*), 3.78 (broad singlet, 2H, CH_2), 1.95 (unresolved quintet, 2H, CH_2), 1.38 (m, 2H, 2 × CH_2), 1.27 (m, 16H, 10 × CH_2), 0.88 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.1, 189.8, 187.1, and 186.6 (4 × *C*═O), 143.0, 137.4, 137.3, 137.2, 137.0, and 135.3 (6 × sp^2 *tertiary* C and *C* aromatic), 134.5 and 133.9 (2 × *C*H aromatic, DEPT), 133.5 (sp^2 *tertiary* C), 132.9 and 132.8 (2 × *C*H aromatic, DEPT), 132.5 (sp^2 *tertiary* C), 129.9, 129.6, 128.8, 128.7, 128.6, 128.3, and 128.2 (7 × *C*H aromatic, DEPT), 71.1 (*quaternary* C), 58.0, 53.3, 31.9, 29.7, 29.6, 29.5, 29.3, 28.0, 27.3, 22.6 (10 × *C*H_2, DEPT), 14.1 (*C*H_3, DEPT); IR (KBr, cm^{-1}) ν 2923, 2852, 1663 (C═O), 1596, 1578, 1539, 1448, 1258, 1242; MS (FAB+) *m/z* 1416 (M + 1, 9), 1309 (1), 1118 (2), 531 (2), 207 (15), 147 (25), 133 (15), 105 ($PhCO^+$, 100). Anal. Calcd for $C_{82}H_{65}NO_8S_7$: C, 69.51; H, 4.62; N, 0.99. Found: C, 69.38; H, 4.66; N, 0.97.

2-(4,5-Dibenzoyl-1,3-dithiol-2-ylidenyl)-2-[3-(4,5-dibenzoyl-1,3-dithiol-2-ylidenyl)-5,6-dihydro-2-thioxo[1,4]-thiazin-4-yl]ethanethial 12. DBA (35 mg, 0.150 mmol) was added to a solution of 5,6-dihydro-4-(3-thiono[1,2]dithiol-4-yl)-[1,2]dithiolo[3,4-*b*][1,4]thiazine-3-thione **11** (20 mg, 0.059 mmol) in benzene (5 mL), and the resulting solution was stirred at room temperature for 20 min. The solvent was removed in the rotary evaporator at room temperature. The resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 1:1) to give **12** as a brown solid (22 mg, 0.028 mmol, 47%), mp 118−119 °C (dec) (CH_2Cl_2−petroleum ether). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.74 (s, 1H, S═C*H*), 7.48 (m, 10H, 2 × C_6H_5), 7.25 (m, 10H, 2 × C_6H_5), 4.12 (m, 1H, $^1/_2CH_2$), 3.63 (m, 1H, $^1/_2CH_2$), 3.44 (m, 1H, $^1/_2CH_2$), 3.08 (m, 1H, $^1/_2CH_2$); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 199.2 (S═*C*H, DEPT), 197.7 (*C*═S), 187.6, 187.2, and 187.1 (3 × *C*═O), 159.9, 155.8, 142.9, 141.3,

140.6, 140.2, 137.3, 137.2, 136.0 (9 × sp^2 *tertiary* C and *C* aromatic), 134.7, 134.6, 134.5 (3 × *C*H aromatic, DEPT), 133.8 (sp^2 *tertiary* C), 129.5, 129.4, 129.3, and 129.2 (4 × *C*H aromatic, DEPT), 46.2 (*C*H$_2$, DEPT), 33.0 (*C*H$_2$, DEPT); IR (KBr, cm^{-1}) ν 2923, 1662, 1654 (C=O), 1647, 1595, 1447, 1261 (C=S), 1231 (C=S), 692; MS (FAB+) *m*/*z* 808 (M + 1, 2), 105 (PhCO$^+$, 50), 77 (Ph$^+$, 45), 69 (70), 55 (100).

Reaction of [1,2]Dithiolo[1,4]thiazine 11 and 3.5 equiv of DBA. DBA (60 mg, 0.256 mmol) was added to a solution of **11** (25 mg, 0.074 mmol) in benzene (5 mL), and the resulting solution was stirred at room temperature for 45 min. The solvent was removed in the rotary evaporator at room temperature, and the resulting solid was purified by flash chromatography (petroleum ether−CH_2Cl_2 1:1) to give **13** as a brown solid (CH_2Cl_2−petroleum ether) (34 mg, 0.033 mmol, 44%) and **14** as an orange solid (17 mg, 0.016 mmol, 22%) (CH_2Cl_2−petroleum ether).

2-(4,5-Dibenzoyl-1,3-dithiol-2-ylidenyl)-6-{3,4-dibenzoyl-7,8-dihydro-5-[spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)]thiopyrano[2,3-*b*][1,4]thiazine]-6-yl}-ethanethial 13. mp 109−110 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.87 (s, 1H, S=C*H*), 8.06−6.95 (m, 30H, 6 × C_6H_5), 4.00 (two partially resolved triplets, J = 13.6 Hz, J = 2.1 Hz, 1H, $^1/_2$C*H*$_2$), 3.36 (t, J = 12.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.27 (doubled triplet, J = 12.0 Hz, J = 2.1 Hz, 1H, $^1/_2$C*H*$_2$), 3.11 (d, J = 13.6 Hz, 1H, $^1/_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.8 (S=*C*H, DEPT), 193.0, 189.8, 187.3, 187.1, and 186.5 (5 × *C*=O), 160.5, 142.8, 140.9, 140.6, 138.6, 137.3, 137.1, 137.0, 136.9, 136.8, 136.3, 135.4, and 135.3 (13 × sp^2 *tertiary* C and *C* aromatic), 134.3, 134.0, 133.9, 133.8, 133.5, 133.1, 133.0, 130.1, 129.9, 129.7, 129.2, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, and 128.1 (18 × *C*H aromatic, DEPT), 120.0 (sp^2 *tertiary* C), 68.1 (*quaternary* C), 49.2 and 26.6 (2 × *C*H$_2$, DEPT); IR (KBr, cm^{-1}) ν 2923, 1655 (C=O), 1649, 1595, 1447, 1260 (C=S), 1177, 692; MS (FAB+) *m*/*z* 1042 (M + 1, 42), 711 (49), 698 (39), 638 (46), 105 (PhCO$^+$, 70), 69 (80), 55 (100). Anal. Calcd for $C_{56}H_{35}NO_6S_7$: C, 64.53; H, 3.38; N, 1.34. Found: C, 64.36; H, 3.54; N, 1.23.

3-(4,5-Dibenzoyl-1,3-dithiol-2-ylidenyl)-4-[5,6-dibenzoyl-4-{spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)}thiopyran-3-yl]-5,6-dihydro[1,4]thiazine-2-thione 14. mp 116−117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07−6.97 (m, 30H, 6 × C_6H_5), 6.43 (s, 1H, *H*C=C), 5.23 (m, br, 1H, $^1/_2$C*H*$_2$), 3.90 (m, br, 1H, $^1/_2$C*H*$_2$), 3.73 (m, br, 1H, $^1/_2$C*H*$_2$), 3.14 (m, br, 1H, $^1/_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.2 (*C*=S), 193.4, 190.8, 187.3, 186.9, and 186.3 (5 × *C*=O), 159.2, 141.5, 140.1, 137.4, 136.7, 136.4, and 135.4 (7 × sp^2 *tertiary* C and *C* aromatic), 134.6, 134.1, 134.0, and 133.4 (4 × *C*H aromatic, DEPT), 132.9 (sp^2 *tertiary* C), 130.3, 130.1, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, and 128.1 (12 × *C*H aromatic, DEPT), 110.5 (sp^2 *tertiary* C), 67.5 (*quaternary* C), 48.8 (*C*H$_2$, DEPT), 26.7 (*C*H$_2$, DEPT); IR (KBr, cm^{-1}) ν 2924, 1655 (C=O), 1595, 1448, 1260, and 1230 (C=S), 1177, 690; MS (FAB+) *m*/*z* 1042 (M + 1, 7), 711 (3), 105 (PhCO$^+$, 50), 69 (80), 55 (100). Anal. Calcd for $C_{56}H_{35}NO_6S_7$: C, 64.53; H, 3.38; N, 1.34. Found: C, 64.87; H, 3.66; N, 1.19.

3,4-Dibenzoyl-6-[5,6-dibenzoyl-4-{spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)}-thiopyran-5-yl]-7,8-dihydro-5-[spiro(4,5-dibenzoyl-1,3-dithiol-2-yl)]thiopyrano[2,3-*b*][1,4]-thiazine 15a. DBA (69 mg, 0.295 mmol) was added to a solution of **11** (20 mg, 0.059 mmol) in benzene (10 mL), and the resulting solution was stirred under reflux for 60 min. A new portion of DBA was then added (20 mg, 0.085 mmol), and the resulting solution was stirred under reflux for 30 min. This latter process was repeated two additional times. The solvent was removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (CH_2Cl_2–petroleum ether 1:1 to CH_2Cl_2) to give **15** as a yellow solid (CH_2Cl_2–petroleum ether) (55 mg, 0.043 mmol, 73%), mp 209−210 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00−6.88 (m, 40H, 8 × C_6H_5), 6.31 (s, 1H, *H*C=C), 5.34 (dt, J = 13.0 Hz, J = 3.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.59 (dt, J = 12.0 Hz, J = 3.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.50 (triplet, J = 13.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.32 (d, J = 12.0 Hz, 1H, $^1/_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.0, 192.3, 191.1, 189.6, 188.1, 187.2, 187.1, and 186.8 (8 × *C*=O), 139.5, 137.4, 137.3, 136.8, 136.7, 135.9, 135.3, 134.9, 134.8 (9 × sp^2 *tertiary* C and *C* aromatic), 134.4, 134.1, 133.8, 133.5, 133.3, 133.2, 133.0, 132.7, and 132.4 (9 × *C*H aromatic, DEPT), 132.2 (sp^2 *tertiary* C), 130.4, 130.1, 129.6, 129.5, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, and 128.1 (15 × *C*H aromatic, DEPT), 125.5 (sp^2 *tertiary* C), 69.6 and 67.7 (2 × *quaternary* C), 49.5 (*C*H$_2$, DEPT), 25.8 (*C*H$_2$, DEPT); IR (KBr, cm^{-1}) ν 3060, 2924, 1660 (C=O), 1595, 1579, 1534, 1448, 1258, 1173, 691; MS (FAB+) *m*/*z* 1275 (M$^+$, 10), 1169 (1), 1009 (2), 711 (2), 679 (2), 105 (PhCO$^+$, 100). Anal. Calcd for $C_{72}H_{45}NO_8S_7$: C, 67.74; H, 3.55; N, 1.10. Found: C, 67.57; H, 3.49; N, 1.14.

3,4-Di(2-thienoyl)-6-[5,6-di(2-thienoyl)-4-{spiro[4,5-di-(2-thienoyl)-1,3-dithiol-2-yl]}-thiopyran-5-yl]-7,8-dihydro-5-[spiro{4,5-di(2-thienoyl)-1,3-dithiol-2-yl}]thiopyrano-[2,3-*b*][1,4]thiazine 15b. Di(2-thienoyl)acetylene,[19] DTA (106 mg, 0.43 mmol), was added to a solution of **11** (29 mg, 0.085 mmol) in toluene (10 mL), and the resulting solution was stirred under reflux for 60 min. The solvent was removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (CH_2Cl_2−petroleum ether 1:1 to CH_2Cl_2−AcOEt 1:0.04) to give **15b** as an orange solid (CH_2Cl_2−petroleum ether) (88 mg, 0.066 mmol, 78%), mp 159−160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.40−6.74 (m, 24H, 8 × C_4H_3S), 6.63 (s, br, $^1/_2$H, *H*C=C), 6.30 (s, br, $^1/_2$H, *H*C=C), 5.34 (dt, J = 12.0 Hz, J = 2.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.57 (d, J = 12.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.46 (dt, J = 12.0 Hz, J = 2.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.33 (d, J = 12.0 Hz, 1H, $^1/_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.8, 181.2, 179.1, 178.9, 178.5, 178.4, 178.3, 178.1 (8 × *C*=O), 143.3, 143.2, 141.3, 138.2, 138.1, 138.0, 137.9, 137.8, 137.3, 137.2, 137.0, 136.5, 136.4, 135.9, 135.5, 135.4, 135.2, 135.0, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, and 127.8 (25 × sp^2 *tertiary* C, *C* and *C*H aromatic), 62.7 (*quaternary* C), 49.4 (*C*H$_2$), 29.7 (*C*H$_2$); IR (KBr, cm^{-1}) ν 3089, 2924, 1634 (C=O), 1537, 1511, 1408, 1262, 723; MS (FAB+) *m*/*z* 1324 (M + 1, 20), 703 (10). HRMS (FAB+) (M + 1)$_{found}$ = 1323.7742. $C_{56}H_{30}NO_8S_{15}^+$ requires 1323.7782. Anal. Calcd for $C_{56}H_{29}NO_8S_{15}$: C, 50.77; H, 2.21; N, 1.06. Found: C, 50.73; H, 2.18; N, 1.00.

3,4-Di(2-furoyl)-6-[5,6-di(2-furoyl)-4-{spiro[4,5-di(2-furoyl)-1,3-dithiol-2-yl]}-thiopyran-5-yl]-7,8-dihydro-5-[spiro{4,5-di(2-furoyl)-1,3-dithiol-2-yl}]thiopyrano[2,3-*b*]-[1,4]thiazine 15c. Di(2-furoyl)acetylene, DFA, was prepared in three steps from furfural (61% overall yield) following a general method[12b] [dark yellow solid, mp 146−147 °C]. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.74 (s, 2H aromat), 7.50 (d, J = 4 Hz, 2H aromat), 6.65 (d, J = 4.0 Hz, 2H aromat); IR (neat, cm^{-1}) ν 1634 (C=O), 1462; MS (EI) *m*/*z* 214 (M$^+$, 100)]; DFA (250 mg, 1.17 mmol) was added to a solution of **11** (78 mg, 0.23 mmol) in toluene (10 mL), and the resulting solution was stirred under reflux for 60 min. The solvent was removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (CH_2Cl_2−petroleum ether 1:1 to CH_2Cl_2−AcOEt 1:1) to give **15c** as a dark yellow solid (CH_2Cl_2−petroleum ether) (151 mg, 0.127 mmol, 55%), mp 169−170 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60−7.20 (m, 16H, 8 × C_4H_3O), 6.57−6.29 (m, 8H, 8 × C_4H_3O), 6.11 (s, 1H, *H*C=C), 5.20 (d, J = 14.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.52 (d, J = 14.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.36 (t, J = 14.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.26 (d, J = 14.0 Hz, 1H, $^1/_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.0, 178.0, 176.5, 175.4, 173.3, 173.0, 172.5, and 172.4 (8 × *C*=O), 151.1, 151.0, 150.2, 149.3, 149.1, 149.0, 148.7, 148.5, 148.2, 148.0, 147.6, 125.3, 123.0, 122.9, 122.8, 122.7, 122.6, 122.5, 122.4, 122.0, 121.9, 121.6, 121.4, 121.2, 120.9, 120.8, 120.7, 120.6, 113.1, 112.7 (30 × sp^2 *tertiary* C, *C* and *C*H aromatic), 66.5 (*quaternary* C), 49.5 (*C*H$_2$), 29.6 (*C*H$_2$); IR (KBr, cm^{-1}) ν 3127, 2963, 1651 (C=O), 1563, 1537, 1460, 1390, 1289, 1082, 1020, 765; MS (FAB+) *m*/*z* 1196 (M + 1, 100), 918 (35), 643 (55). HRMS (FAB+) (M + 1)$_{found}$ = 1195.9608. $C_{56}H_{30}NO_{16}S_7^+$ requires 1195.9610. Anal. Calcd for $C_{56}H_{29}NO_{16}S_7 \cdot 1.5CH_2Cl_2$: C, 52.17; H, 2.44; N, 1.06. Found: C, 52.51; H, 2.49; N, 1.06.

3,4-Di(thianaphthen-3-ylcarbonyl)-6-[5,6-di(thianaphthen-3-ylcarbonyl)-4-{spiro[4,5-di(thianaphthen-3-ylcarbonyl)-1,3-dithiol-2-yl]}-thiopyran-5-yl]-7,8-dihydro-5-[spiro{4,5-di(thianaphthen-3-ylcarbonyl)-1,3-dithiol-2-yl}]thiopyrano[2,3-*b*][1,4]thiazine 15d. Di(thianaphthen-3-ylcarbonyl)acetylene, DTNA, was prepared in three steps from thianaphthene-3-carboxaldehyde (57% overall yield) following a general method[12b] [yellow solid, mp 189−190 °C]. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.78 (m, 2H aromat), 7.89 (m, 2H aromat), 7.57 (m, 6H aromat); IR (KBr, cm^{-1}) ν 1632 (C═O), 1202; MS (EI) *m*/*z* 346 (M^+, 100)]; DTNA (236 mg, 0.68 mmol) was added to a solution of **11** (51 mg, 0.15 mmol) in toluene (10 mL), and the resulting solution was stirred under reflux for 60 min. The solvent was removed in the rotary evaporator, and the resulting solid was purified by flash chromatography (petroleum ether to petroleum ether−CH_2Cl_2 1:0.3) to give **15d** as a dark yellow solid (CH_2Cl_2−petroleum ether) (176 mg, 0.102 mmol, 68%), mp 180−181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65−6.91 (m, 40H, 8 × C_8H_5S), 6.38 (s, 1H, *H*C═C), 5.48 (d, J = 14.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.73 (t, J = 12.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.59 (t, J = 14.0 Hz, 1H, $^1/_2$C*H*$_2$), 3.44 (d, J = 12.0 Hz, 1H, $^1/_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.9, 186.4, 184.0, 183.8, 181.3, 181.1, 180.9, and 180.6 (8 × *C*═O) (29 × sp^2 *tertiary* C, *C* and *C*H aromatic), 67.3 and 66.9 (2 × *quaternary* C), 49.7 (*C*H$_2$), 29.7 (*C*H$_2$); IR (KBr, cm^{-1}) ν 3084, 2918, 1634 (C═O), 1532, 1537, 1487, 1458, 1420, 1196, 757, 731; MS (FAB+) *m*/*z* 1724 (M + 1, 100), 1314 (20), 903 (35). HRMS (FAB+) $(M + 1)_{found}$ = 1723.9095. $C_{88}H_{46}NO_8S_{15}^+$ requires 1723.9034. Anal. Calcd for $C_{88}H_{45}NO_8S_{15}\cdot 3CH_2Cl_2$: C, 55.29; H, 2.60; N, 0.71. Found: C, 55.68; H, 2.65; N, 0.71.

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Supporting Information Available: ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR (CD_2Cl_2, 75 MHz) spectra of **12**. Vibrational analysis, semiempirical (PM3, RHF, conjugate gradient algorithm of Polak−Ribiere), for molecules **10a**(**A**−**D**) and **15a**, by singlet state calculations of energies and gradient, eigenvalues, atomic orbital electron populations, net charges and coordinates, atomic gradients, force constant matrix, normal-mode frequencies of vibration, and integrated infrared band intensities of the IR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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