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Synthesis of Pyrrolidine-Fused 1,3-Dithiolane Oligomers by the Cycloaddition of Polycyclic Dithiolethiones to Maleimides and Evaluation as Mercury(II) Indicators

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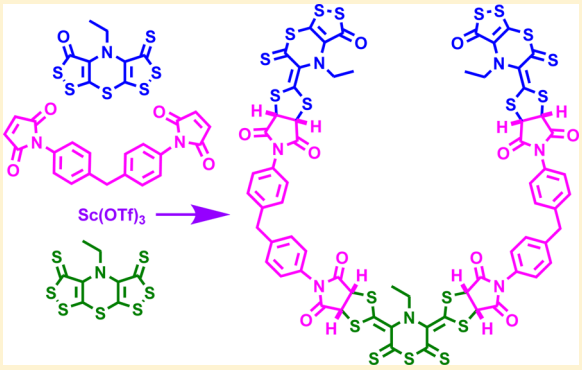
Supporting Information

ABSTRACT: The scandium triflate-catalyzed cycloaddition reaction of polycyclic 1,2-dithiolethiones to maleimides is described. The reaction constitutes an easy approach to linear as well as branched oligomeric *cis*-fused dihydro[1,3]dithiolo[4,5-*c*]pyrrole-4,6-dione rings interconnected by 3,5-diylidenethiomorpholine-2,6-dithione or ylidene-6-thioxo[1,2]dithiolo[3,4-*b*][1,4]thiazin-3-one groups. The presence of highly colored, highly polarized push−pull α,β-unsaturated thione groups in their structures make these compounds sensitive to the presence of mercury(II) cation in organic or mixed organic/aqueous solvents.



INTRODUCTION

Polyheterocyclic compounds bearing 1,3-dithiole[1] and 1,3-dithiolane[2] moieties are important donor units in new electronic materials and molecular devices such as extended tetrathiafulvalene derivatives,[3] organic superconductors,[4] push−pull chromophores,[5] switchable organic materials,[6] receptors,[7] shape-persistent macrocycles, and conducting polymer wires.[8] Despite the enormous synthetic efforts in the search for these new materials, the number of methods currently used for this chemistry is surprisingly low, being conserved unchanged for a long time.[9] Less common synthetic methods for the preparation of 1,3-dithiole derivatives include 1,3-dipolar cycloadditions of 1,2-dithiole-3-thiones and activated triple bonds, which permit multiple cycloadditions in one pot, thereby giving rise to extended TTF derivatives by very short reaction pathways.[10] Despite the rich chemistry shown by these reactions, related alternatives are scarce. Thus, the photochemical reactions of 1,2-dithiole-3-thiones and nonactivated alkenes are known to give unstable adducts that can be trapped by dienophiles such as *N*-phenylmaleimide.[11] Notwithstanding the extensive chemistry developed in the field of 1,2-dithiole-3-thiones,[12] their cycloaddition reactions with classical activated double bonds such as maleimides are not known. The only loosely related known reaction is a single example of a thermal cycloaddition of 2,4-diphenylisothiazoline-5-thione and *N*-phenylmaleimide that was reported long time ago by McKinnon and co-workers.[13] Apparently, the thermal reaction of *N*-substituted maleimides and 1,2-dithiole-3-thiones does not work under heating in high-boiling-point solvents. Such a reaction, if it should be possible, would constitute a very good approach to dihydro derivatives of the 2-methylene-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione system, an almost unknown system[14] that could be potentially useful in the search for new materials and pharmacological leads. Therefore, in this paper we describe the scandium triflate-catalyzed cycloaddition of polycyclic dithiolethiones to maleimides as an unprecedented approach to branched oligomeric polyheterocyclic 1,3-dithiolanes.

RESULTS AND DISCUSSION

We selected a suitable catalyst, scandium triflate, which was very effective for the 1,3-cycloaddition reactions of polyheterocyclic dithiolethiones and activated alkynes,[15] to study the cycloaddition reaction of the most reactive dithiolethiones we had in hand and commercial or easily synthesized maleimides. Our starting materials, 4-alkylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazin-3-oxo-5-thiones and -3,5-dithiones can be prepared in one-pot reactions from Hünig's base or *N*,*N*-(diisopropyl)-benzylamine in a selective fashion and therefore are fast entries to complex heterocyclic chemistry.[10a] We first selected to use 4-ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione[16] (**1**) in catalyzed reactions with commercial maleimides **2a**−**j**. In this way, **1** and **2a**−**j** reacted equimolecularly in refluxing dichloromethane for 1 h in the presence of scandium triflate (25% mol) to give, after workup and column chromatography, the corresponding orange solid adducts, 5-substituted 2-(4-ethyl-3-oxo-6-thioxo[1,2]dithiolo[3,4-*b*][1,4]thiazin-5-ylidene)-

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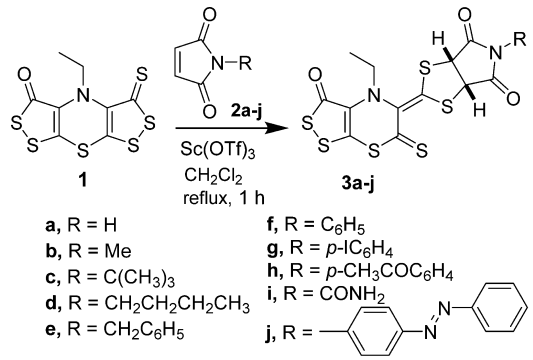
dihydro[1,3]dithiolo[4,5-*c*]pyrrole-4,6-diones **3a**–**j**, in yields of up to 88% (Scheme 1).

Scheme 1. Reaction of Bisdithioloketothione 1 and Maleimides 2a–j



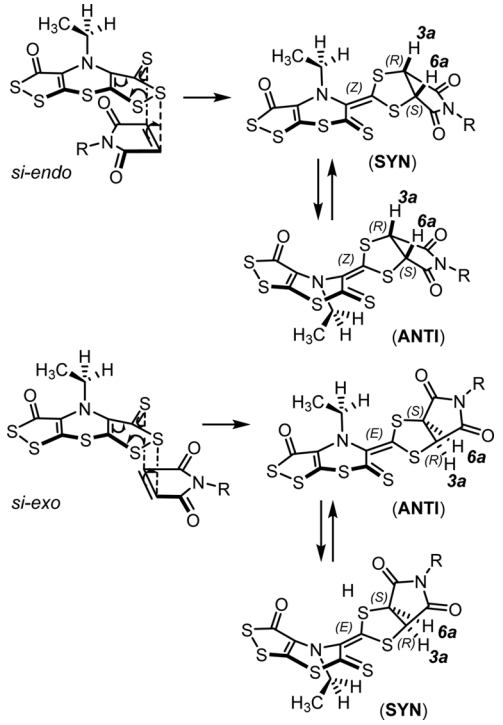
Entry	Maleimide	Cycloadduct	Yield[a] [%]	Conformers ratio
a	**2a**	**3a**	68	61/39
b	**2b**	**3b**	77	57/43
c	**2c**	**3c**	81	52/48
d	**2d**	**3d**	88	52/48
e	**2e**	**3e**	52	52/48
f	**2f**	**3f**	64	53/47
g	**2g**	**3g**	72	55/45
h	**2h**	**3h**	59	55/45
i	**2i**	**3i**	38	58/42
j	**2j**	**3j**	51	55/45

[a]Isolated yields.

All of the obtained compounds showed a single spot on the TLC silica plates, but their ^{1}H NMR spectra clearly showed two sets of signals, each composed of two doublets at δ 4.5–6.0, corresponding the C3a and C6a protons (the pair of *cis*-bridgehead protons in the dithiolopyrrole system) for every compound, in a roughly equimolecular amount, and two complex multiplets for the signals of the methylene protons of the ethyl group. Therefore, the complex ^{1}H NMR spectra are due to the slow inversion of the pyramidal nitrogen in the 1,4-thiazine ring and consequently to the presence of nitrogen inversion conformers. Two chiral centers at the C3a and C6a positions are generated by the 1,3-dipolar cycloaddition reaction with the maleimide, causing the α-methylene hydrogen atoms of the *N*-substituent of the starting substrate **1** to become diastereotopic in the cycloadduct and thus to show magnetic nonequivalence in the ^{1}H NMR spectra. Therefore, the two protons of the dithiolopyrrole system (H3a and H6a) are structurally nonequivalent. Indeed both the *endo*- and *exo*-1,3-dipolar cycloaddition reactions lead to enantiomeric dithiolopyrrole rings (Scheme 2). In a characteristic example, compound **3f** showed a set of two partially superposed sextets centered at δ 3.24 (ddq, J = 25.9, 14.2, 6.9 Hz) for one methylene proton and another set of two partially superposed sextets centered at δ 3.56 (ddq, J = 24.7, 14.6, 7.3 Hz) for the other methylene proton along with four doublets, two at δ 5.28 and 5.02 (J = 8.5 Hz) for the pair of dithiolopyrrole protons of one conformer and two at δ 5.18 and 4.81 (J = 9.0 Hz) for the pair of dithiolopyrrole protons of the other conformer.

The transformation among the conformational isomers SYN and ANTI was studied by DFT calculations performed on a simplified model of compounds **3a**–**j**. The SYN/ANTI transformation can be explained as an inversion of the configuration of the amine nitrogen atom. In order to avoid complications arising from the simultaneous inversion on the nitrogen atom and the rotation of the C–C bond in the ethyl group, this ethyl group was simplified to a methyl group. In these theoretical calculations, we found that for this simplified model of **3a**–**j** the SYN and ANTI conformers have similar stabilities, with a free energy difference of 0.319 kcal·mol^{-1}. This small difference is in good agreement with the experimental observation of both conformers in solution, and on the basis of the calculated free energy difference between the conformers, the statistical distribution of the population at 298 K is 63.2% for the ANTI conformer and 36.8% for the SYN conformer (Figure 1). The estimated barrier for the SYN/ANTI transformation in the simplified model is 17.6 kcal/mol, which is high enough to allow the observation of both isomers in the ^{1}H NMR experiments at room temperature.[17] Similar calculations performed on a nonsimplified structure of compound **3a** afforded populations of 62.7% for ANTI-**3a** and 37.3% for SYN-**3a** (61/39 experimental), in good agreement with the experimental results (Figure 2).

Scheme 2. Mechanism of the Reaction between Bisdithioloketothione 1 and Maleimides and Nitrogen Inversion of the 1,4-Thiazine Ring



All of these compounds decomposed at the melting point in a cycloreversion reaction followed by thermal desulfuration, giving rise to 4-ethylbis[1,2]dithiolo[4,3-*b*:3′,4′-*d*]pyrrole-3-oxo-5-thione (**4**), a known product of thermal desulfuration of **1**[16b] (Scheme 3). As a characteristic example, upon slow melting of **3c** in a heating chamber under a microscope, yellow crystals of **4** were formed by sublimation as **3c** melted. Compound **4** was characterized by mass spectrometry and compared to a synthetic sample.

In the same way, 4-benzylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazin-3-oxo-5-thione[18] (**5**) and commercial maleimides **2a**–**c**,**e**–**g** reacted equimolecularly in refluxing dichloromethane for 2–4 h in the presence of scandium triflate (25% mol) to give, after workup and column chromatography, the corresponding

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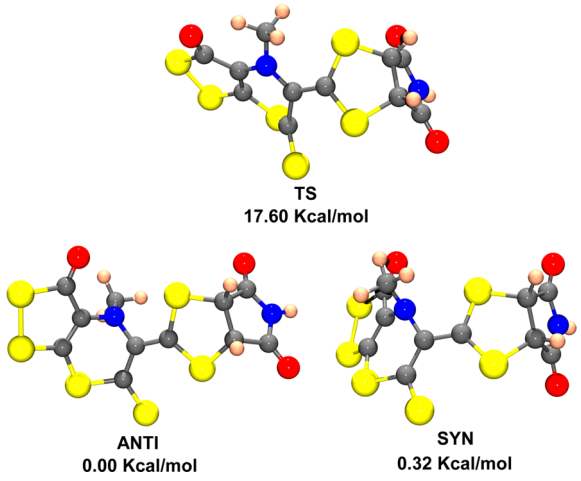


Figure 1. DFT-calculated structures of the SYN and ANTI conformers and of the transition state (TS) for the SYN/ANTI transformation of a model compound.

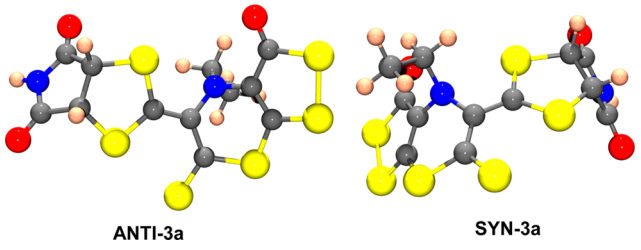
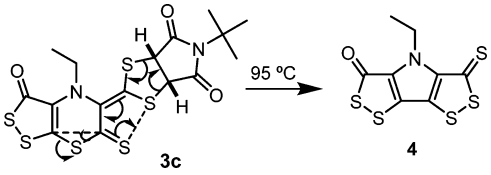


Figure 2. DFT-calculated structures of the ANTI and SYN conformers of **3a**.

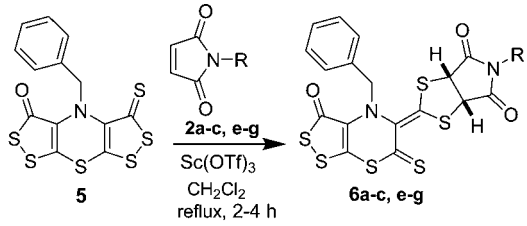
Scheme 3. Thermal Decomposition of 3c



orange solid adducts, 5-substituted 2-(4-benzyl-3-oxo-6-thioxo-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5-ylidene)dihydro[1,3]-dithiolo[4,5-*c*]pyrrole-4,6-diones **6a–c,e–g**, in yields of up to 74% (Scheme 4). In this case, the inversion of the pyramidal nitrogen in the 1,4-thiazine ring was evidenced in the ^{1}H NMR spectra by the presence of two pairs of doublets, one for each of the benzyl methylene protons, and two sets of signals, each composed of two doublets at δ 4.5–6.0, corresponding to the pair of *cis*-dithiolopyrrole protons for every compound, in amounts from equimolecular to 2:1. In a characteristic example, the ^{1}H NMR spectrum of **6f** showed two pairs of doublets at δ 4.40/4.12 (J = 14.1 Hz) and δ 4.37/4.19 (J = 14.1 Hz) in a 2:1 proportion for the two benzyl methylene protons and two pairs of doublets at δ 5.83/5.58 (J = 8.9 Hz) and δ 5.66/5.35 (J = 9.2 Hz) in a 2:1 proportion for the two pairs of dithiolopyrrole protons.

On the other hand, 4-ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]-thiazin-3,5-dithione[16] (**7**) and 2 equiv of commercial maleimides **2b,f,g** reacted in refluxing dichloromethane for 1–2 h in the presence of scandium triflate (25% mol with respect to **2b,f,g**) to give, after workup and column chromatography, the corresponding orange solid adducts, 5,5′-disubstituted 2,2′-(4-ethyl-2,6-

Scheme 4. Reaction of Bisdithioloketothione 5 and Maleimides 2a–c,e–g



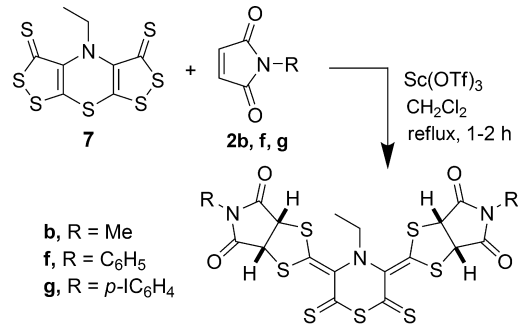
a, R = H **e**, R = $CH_2C_6H_5$
b, R = Me **f**, R = C_6H_5
c, R = $C(CH_3)_3$ **g**, R = *p*-IC_6H_4

Entry	Maleimide	Cycloadduct	Yield[a] [%]	Conformers ratio
a	**2a**	**6a**	67	66/34
b	**2b**	**6b**	70	59/41
c	**2c**	**6c**	74	55/45
e	**2e**	**6e**	66	62/38
f	**2f**	**6f**	51	65/35
g	**2g**	**6g**	48	55/45

[a]Isolated yields.

dithioxothiomorpholine-3,5-diylidene)bis(5-methyl{or aryl}-dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6-dione)s **8b,f,g**, in yields of up to 67% (Scheme 5). In this case, several conformers

Scheme 5. Reaction of Bisdithiolodithione 7 and Maleimides 2b,f,g



Entry	Maleimide	Cycloadduct	Yield[a] [%]
b	**2b**	**8b**	65
f	**2f**	**8f**	67
g	**2g**	**8g**	15

[a]Isolated yields.

are expected, therefore complicating the otherwise simple ^{1}H NMR spectrum of every compound. In this way, the ^{1}H NMR spectrum of **8b** showed four sets of signals (eight doublets) for the dithiolopyrrole protons (δ 5.0–6.0) in different proportions, whereas **8f** showed only two main equimolecular conformers and traces of two others and **8g** showed only one main conformer and traces of two others in the same region of the ^{1}H NMR spectrum, probably for steric reasons.

Moreover, bisdithioloketothione[16] **1** reacted with commercial bismaleimides **9a** and **9b** and the synthesized bismaleimide **9c**[19] in refluxing dichloromethane for 1 h in the presence of scandium triflate (25% mol) to give, after workup and column chromatography, the corresponding orange solid monoadducts

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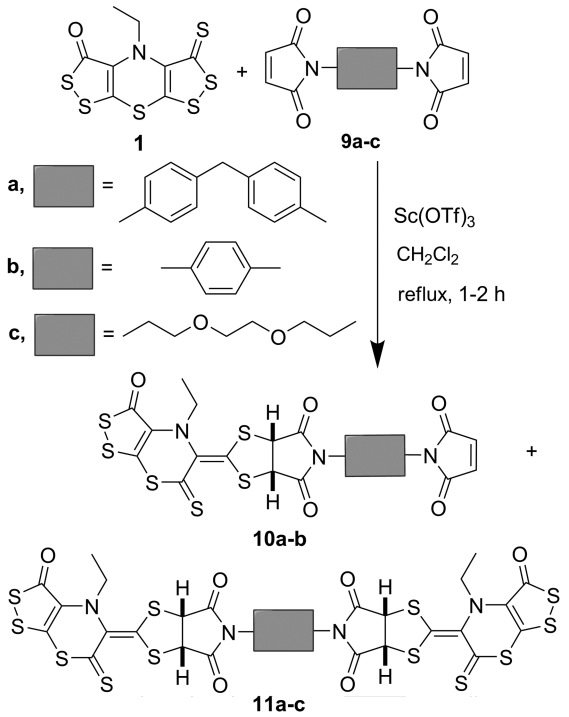
10a and **10b** or the diadducts **11a–c** in yields of up to 55% (Scheme 6). The structures of compounds **10a–b** and **11a–c** are

Scheme 6. Reaction of Bisdithioloketothione 1 and Bismaleimides 9a–c



Entry	Maleimide	No. equiv. 1	Cycloadduct Yield [%][a]	Cycloadduct Yield [%][a]
a	**9a**	**1**	**10a** [56]	**11a** [13]
		2	**10a** [25]	**11a** [55]
b	**9b**	**1**	**10b** [27]	**11b** [17]
		2	**10b** [26]	**11b** [24]
c	**9c**	**2**	-----	**11c** [21]

[a]Isolated yields.

represented in Figure 3. The expected compound **10c** was not isolated, probably because of a lack of stability; therefore, in this case only compound **11c** was obtained. The presence of two dithiolopyrrole heterocycles in **11a–c** was evidenced in the ^{1}H NMR spectra by again the presence of four sets of signals (eight doublets) for the heterocyclic protons (δ 4.5–5.5). In contrast, the presence of only one dithiolopyrrole system in **10a** and **10b** was evidenced in their ^{1}H NMR spectra by the presence of only two sets of signals (four doublets) for the heterocyclic protons (δ 4.5–5.5).

In the case of monoadducts **10**, the presence of a maleimide nucleus makes the products suitable for a second cycloaddition reaction. Therefore, bisdithiolodithione[16] **7** and 2 equiv of maleimide **10a** reacted in refluxing dichloromethane for 6 h in the presence of scandium triflate (25% mol) to give, after workup and column chromatography, the corresponding orange solid adduct **12** in 74% yield (Scheme 7). Some traces of the corresponding monoadduct were also recovered from the column, but the compound was not sufficiently stable for a correct characterization. Compound **12** possesses a remarkable stable structure in which all of the spectroscopic characteristics found in the ^{1}H NMR spectra of compounds **3f–h** and **8f–g** are preserved, showing a complex mixture of conformers.

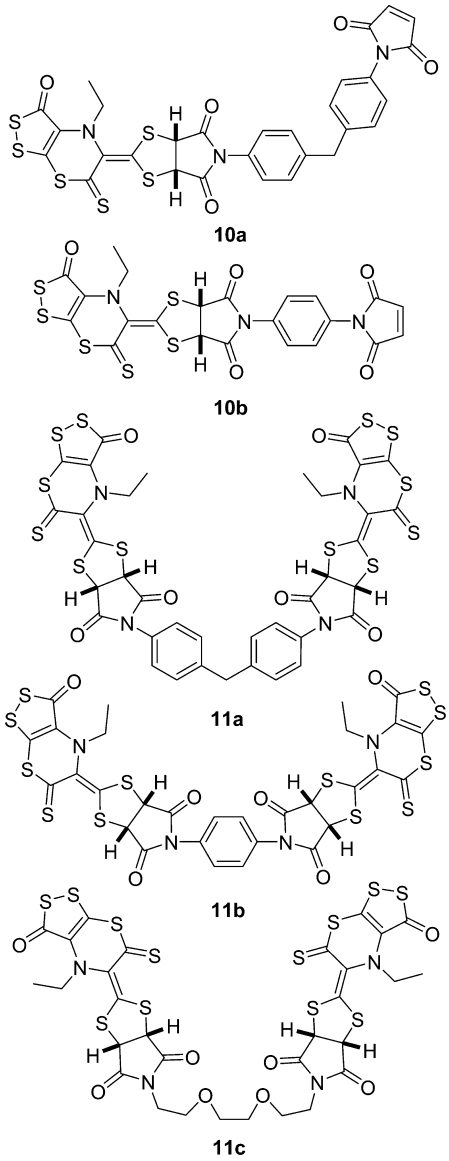


Figure 3. Structures of **10a–b** and **11a–c**.

Furthermore, 1, 2, or 3 equiv of bisdithioloketothione[16] **1** and trismaleimide **13**[20] reacted in refluxing dichloromethane for 4 h in the presence of scandium triflate (25% mol with respect to **1**) to give, after workup and column chromatography, the corresponding orange solid monoadduct **14**, diadduct **15**, or triadduct **16**, respectively, in yields of up to 41% (Scheme 8). Variable amounts of the starting materials and adduct were recovered in each case, and the yields given in Scheme 8 are only for the main product obtained in each reaction. In this case, the yields were lower because of the lack of selectivity, but the compounds were reasonably stable and could be characterized by spectroscopy and microanalysis as in the previous cases.

All of these compounds were obtained within a small window between the reactivity of the starting materials and the stability of the products; this series of reactions was possible because of the presence of scandium triflate as the catalyst of the hitherto unknown 1,3-cycloaddition reaction between dithiolethiones and maleimides. The catalysis permitted the reaction to be performed at a suitable temperature to allow the formation and recovery of the obtained products in almost all cases. These new compounds are thermally sensitive, undergoing a cycloreversion

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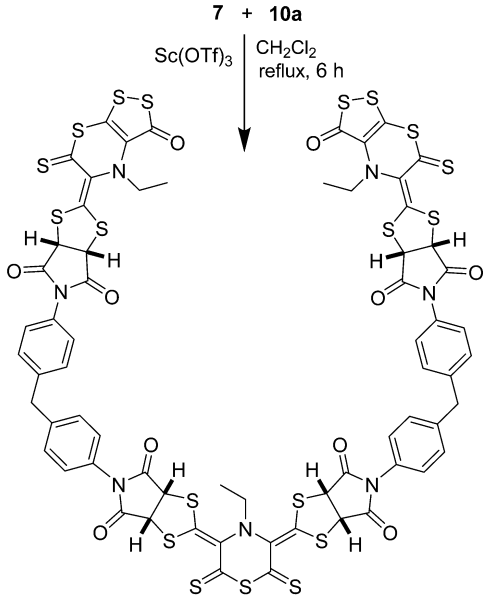
Scheme 7. Synthesis and Structure of 12



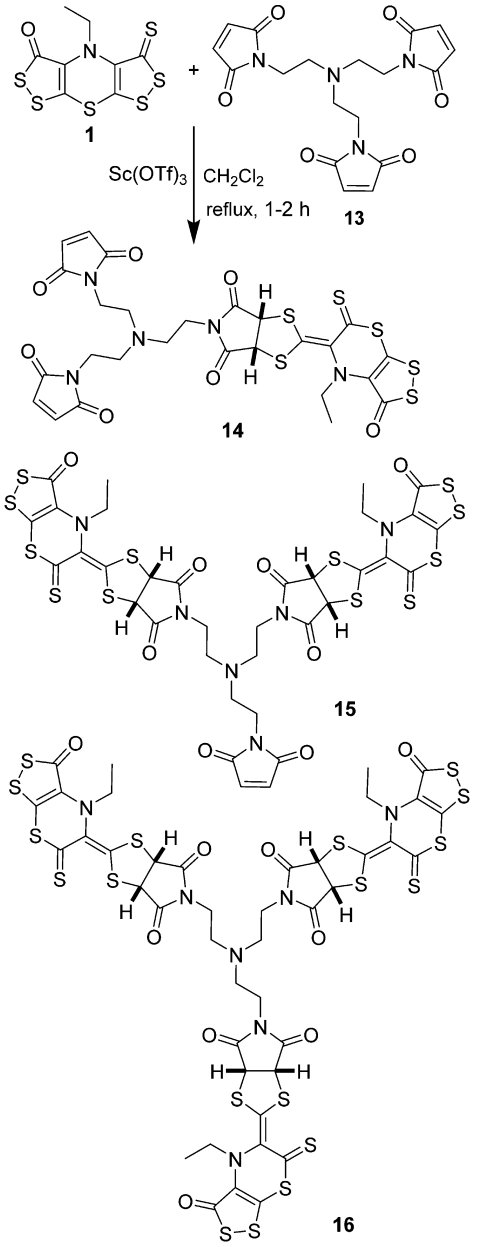
12 (74%)

reaction followed by thermal desulfuration at the melting point. All of these compounds hold in their structure at least one α,β-unsaturated thione group, which is a well-known heterodiene system that is frequently used for hetero-Diels–Alder cycloaddition reactions with activated alkynes.[15] In the present case, all of the attempted reactions under uncatalyzed or catalyzed conditions gave the product of sequential 1,3-dipolar cycloreversion (presumably to give the starting material **1**) followed by the 1,3-dipolar cycloaddition of dithiolethione **1** and the new dipolarophile. In a characteristic example, compound **3f** was subjected to reaction with dibenzoylacetylene (**17**) under diverse conditions[15b] but only the known compound **18**[15b] was obtained with no traces of the expected compound **19** (Scheme 9).

On the other hand, the highly polarized push–pull α,β-unsaturated thione group is responsible for the color exhibited by these compounds. Compounds **3a–j** display an orange color in solution that may undergo changes in the presence of the most common cations or anions. All of them behaved similarly when tested with the same cations or anions, independently of the *N*-alkyl or *N*-aryl group, and therefore, the behavior of two of the most representative examples, **3f** and **8f**, is reported. Addition of 1 equiv or more of Hg^{2+} to 10^{-4} M solutions of **3f** (λ_{max} = 394 nm, ε = 10 946 M^{-1} cm^{-1}) in MeCN resulted in a dramatic change of color from yellow to maroon. This response was selective for Hg^{2+}, and addition of several equivalents of other cations (Ag^{+}, Ni^{2+}, Sn^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Sc^{3+}, and Al^{3+}) as their perchlorate or triflate salts resulted in no appreciable changes (Figure 4).

A quantitative UV–vis titration of a 10^{-4} M solution of **3f** in MeCN with Hg^{2+} (added as the perchlorate salt in MeCN) showed that as Hg^{2+} was added (up to 2 equiv), the original absorption maximum bands centered at 394 and 345 nm decreased and some new bands appeared at 550, 430, and 310 nm, generating isosbestic points at 290, 333, and 402 nm (Figure 5a). After the addition of more than 2 equiv of Hg^{2+}, the new bands slowly decreased with the disappearance of the isosbestic point at 402 nm. The titration profile fitted nicely to a 1:1 binding model (Figure 5b),[21] and the association constant was calculated

Scheme 8. Reaction of Bisdithioloketothione 1 and Trismaleimide 13



Entry	Maleimide	No. equiv.	Cycloadduct	Yield[a] [%]
a	**13**	1	**14**	42
b	**13**	2	**15**	38
c	**13**	3	**16**	43

[a]Isolated yields.

as log K = 4.94 ± 0.09. The Job's plot analysis of the UV–vis titration carried out in MeCN revealed a maximum at a mole fraction of 50% (Figure 5c), in accordance with the proposed 1:1 binding stoichiometry. The Hg^{2+} detection limit of a 10^{-4} M solution of **3f** in MeCN, calculated in UV–vis absorption by the blank variability method,[22] was 3.69 × 10^{-6} M.

The selective sensing action of a 10^{-4} M solution of **8f** in MeCN and 1 equiv or more of Hg^{2+} in MeCN or water was also very effective, in contrast to the lack of effect of adding 1 equiv or

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Scheme 9. 1,3-Dipolar Cycloreversion/Cycloaddition of 3f

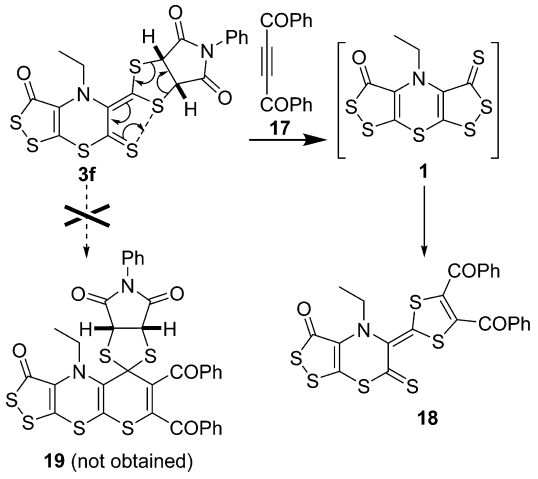

Figure 4. Color changes of 10^{-4} M samples of **3f** in MeCN in the presence of 1 equiv of various cations.

more of other cations (Ag^{+}, Ni^{2+}, Sn^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Sc^{3+}, and Al^{3+}) in MeCN. In this case, a striking color change from yellow to maroon only in the presence of Hg^{2+} was observed (Figure 6).

A quantitative UV−vis titration of a 10^{-4} M solution of **8f** in MeCN with Hg^{2+} (added as the perchlorate salt in MeCN) showed that addition of Hg^{2+} resulted in the decrease of the original absorption maximum bands centered at 390 and 417 nm and the appearance of a large absorption band from 300 to 600 nm (responsible for the observed color) with no appearance of isosbestic points (Figure 7a). Related titrations performed in acetonitrile/water mixtures showed a similar tendency, but a clear isosbestic point at 365 nm was observed (Figure 7b), thus confirming the appearance of a unique equilibrium complex. The titration profile fitted nicely to a 2:1 binding model (Figure 7c),[21] and the association constants were calculated as $\log K_1 = 3.42 \pm 0.14$ and $\log K_2 = 4.56 \pm 0.17$. The Job's plot analysis of the UV−vis titration carried out in MeCN revealed a maximum between mole fractions of 0.60 and 0.70 (Figure 7d), in accordance with the proposed 2:1 binding stoichiometry. The Hg^{2+} detection limit of a 10^{-4} M solution of **8f** in MeCN, calculated in UV−vis absorption by the blank variability method,[22] was 3.16×10^{-7} M, so **8f** showed better performance than **3f**.

In agreement with previous related chromogenic probes for mercury(II) cation, we assumed that in both cases complexation was probably effected through the thione group, leading to the formation of complexes in which Hg^{2+} extends the conjugation between the 1,3-dithiolane and thione groups, causing in both cases bathochromic shifts of the main UV−vis absorption band in UV−visible. As a representative example, the structure of the complex **3f**$[Hg^{2+}]$·MeCN was obtained by DFT calculations (Figure 8). The model found with ligand **3f** and a mercury(II) cation showed a preference for coordination of the mercury cation to the thione sulfur and a preferred orientation through the sulfur atom of the thiomorpholine moiety.

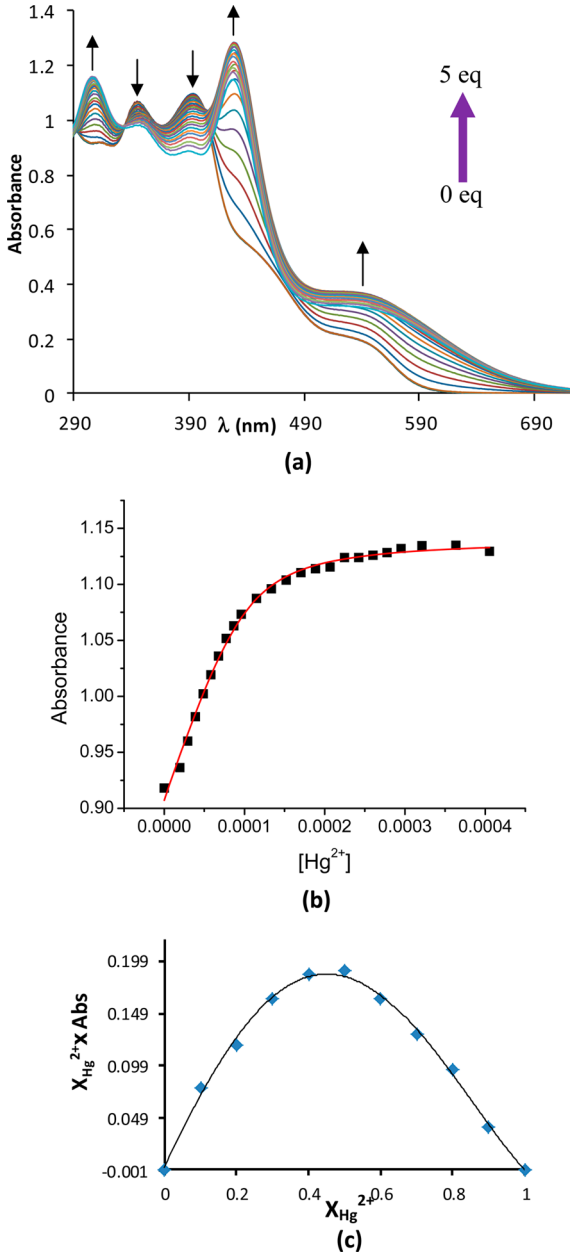

Figure 5. (a) UV−vis titration curves, (b) titration profile (λ_{max} = 312 nm), and (c) Job's plot (λ_{max} = 393 nm) for a 10^{-4} M solution of **3f** in MeCN titrated with Hg^{2+}.

Figure 6. Color changes of 10^{-4} M samples of **8f** in MeCN in the presence of 2 equiv of various cations.

Comparison of the HOMOs and LUMOs of **3f** and **3f**$[Hg^{2+}]$·MeCN showed that the HOMO of **3f** is a nonbonding orbital spread through the 5-(1,3-dithiolan-2-ylidene)[1,2]dithiolo[3,4-*b*][1,4]thiazin-3-oxo-6-thione moiety and the LUMO is an antibonding orbital spread through the 2-(1,3-dithiolan-2-ylidene)dithiocarboxylate moiety. In contrast, the HOMO of **3f**$[Hg^{2+}]$·MeCN is a nonbonding orbital on the *N*-phenyl-

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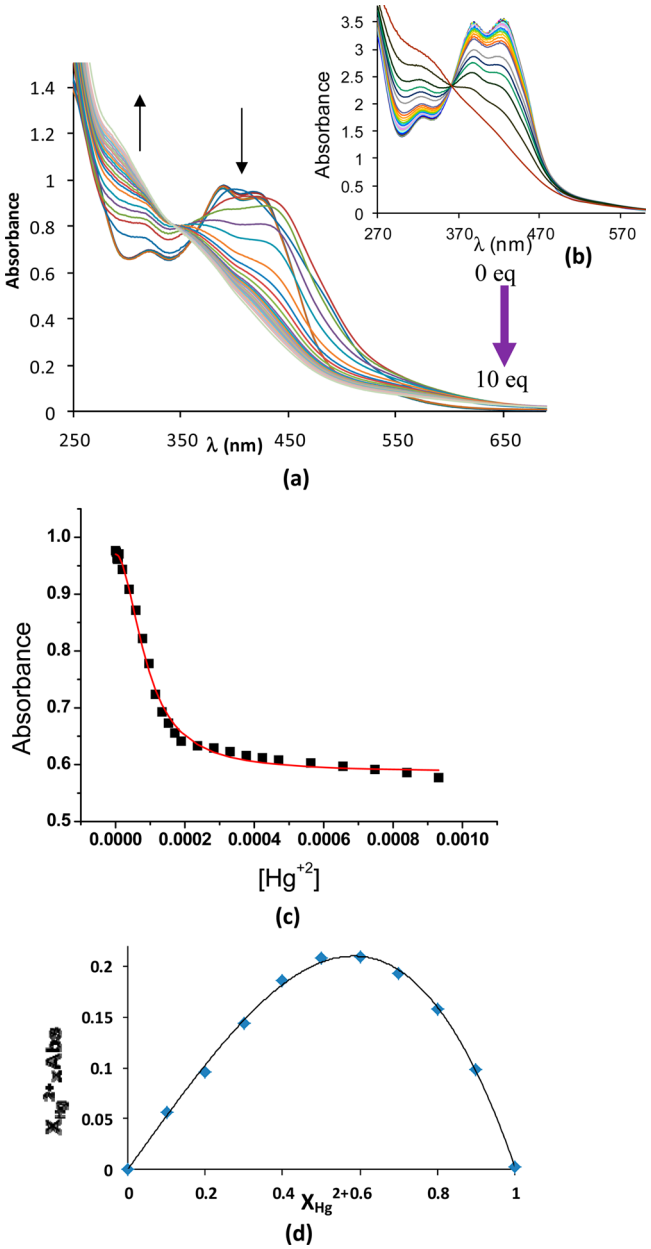

Figure 7. (a, b) Hg^{2+} UV−vis titration curves of (a) 10^{-4} M **8f** in MeCN and (b) 5×10^{-4} M **8f** in MeCN/water. (c) Titration profile (λ_{max} = 390 nm). (d) Job's plot (λ_{max} = 295 nm).

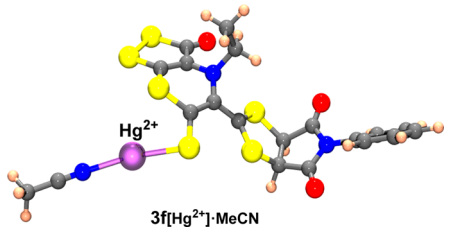

Figure 8. DFT-calculated structure of the complex **3f**[Hg^{2+}]·MeCN.

pyrrolidine-2,5-dione moiety and the LUMO of **3f**[Hg^{2+}]·MeCN is an σ antibonding orbital spread through the 2-(1,3-dithiolan-2-ylidene)dithiocarboxylate−Hg^{2+} moiety (Figure 9), thus proving that the extension of the conjugation between the 1,3-dithiolane group and the complexed thione group is responsible for the bathochromic shift in the UV titration.

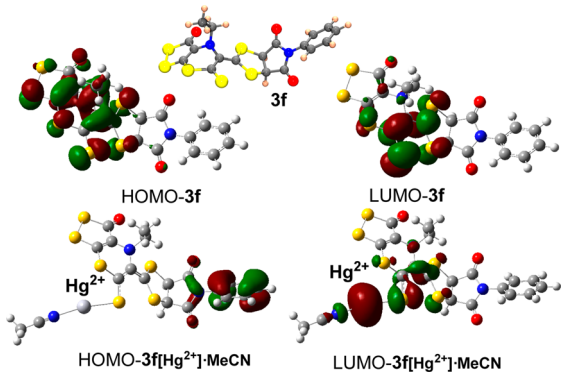

Figure 9. HOMOs and LUMOs of **3f** and the **3f**[Hg^{2+}]·MeCN complex.

CONCLUSION

We have described the scandium triflate-catalyzed cycloaddition of polycyclic dithiolethiones to maleimides. The reaction constitutes an unprecedented approach to linear as well as branched oligomeric *cis*-fused [1,3]dithiolo[4,5-*c*]pyrrole rings interconnected by 3,5-diylidenethiomorpholine-2,6-dithione or ylidene-6-thioxo[1,2]dithiolo[3,4-*b*][1,4]thiazin-3-one groups. Both the 1,4-thiazine core and the *cis*-fused [1,3]dithiolo[4,5-c]pyrrole ring are nonplanar nonaromatic rings that display the presence of inversion conformers of the 1,4-thiazine nitrogen. The presence of highly colored, highly polarized push−pull α,β-unsaturated thione groups in their structures make these compounds sensitive to the presence of mercury(II) cation in organic or mixed organic/aqueous solvents with remarkable selectivity, as shown for two simple derivatives. Therefore, the more structurally complex compounds are good candidates in mercury removal schemes, as absorbants for mercury(II) salts, and as selective indicators. This is due to the enormous number of sulfur heteroatoms (in either acceptor or donor positions) that these new molecular systems display, such as the 1,3-dithiolanes and the conjugated thione groups.

EXPERIMENTAL SECTION

General. The reactions were conducted under dry nitrogen. The solvents were previously distilled under nitrogen over phosphorus pentoxide, calcium hydride, or sodium filaments. Melting points were not corrected. Infrared spectra were registered in potassium bromide tablets. NMR spectra were recorded in DMSO-d_6, $CDCl_3$, CD_3CN, or CD_3OD. Chemical shifts are reported in parts per million with respect to residual solvent protons,[23] and coupling constants ($J_{X-X'}$) are reported in hertz. DEPT experiments from selected samples permitted the assignment of ^{13}C NMR chemical shifts. Elemental analyses of C, H, and N were performed for all new products. High-resolution mass spectra were taken in a quadrupole mass spectrometer by electron impact, FAB, or LSIMS. 4-Ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione[16] (**1**), 4-benzylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione[18] (**5**), 4-ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3,5-dithione[16] (**7**), bismaleimide **9c**,[19] and trismaleimide **13**[20] were prepared following the reported methodologies. Analytical TLC was performed on silica gel 60 plates. Flash column chromatography was carried out on silica gel (0.040−0.063 mm).

General Procedure for the Catalytic Cycloaddition of 4-Ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione (1) and Maleimides 2a−j. Maleimide **2a−j** (1 equiv) and $Sc(OTf)_3$ (19 mg, 0.038 mmol) were added under nitrogen to **1** (50 mg, 0.15 mmol) dissolved in dry dichloromethane (10 mL), and the mixture was refluxed for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica 230−400 mesh, eluting with light petroleum/dichloromethane 60/40 to dichoromethane/ethyl acetate mixtures) to get **3a−j**. Analytical samples

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were obtained by thin-layer chromatography (glass plates, silica 20 cm × 20 cm × 0.1 cm, eluting with dichloromethane/ethyl acetate mixtures).

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3a). 44 mg (68%), orange solid, mp 119−120 °C (dec.) (DCM/EtOAc 1:1), 61/39 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3460, 2853, 1721, 1712, 1631, 1283 cm^{-1}. ^{1}H NMR (CD_3COCD_3, 300 MHz): *δ 10.86 (br s, 0.39H, NH conformer B)*, 10.73 (br s, 0.61H, NH conformer A), 5.63 (d, *J* = 8.6 Hz, 0.61H, CH conformer A), *5.46 (d, J = 9.0 Hz, 0.39H, CH conformer B)*, 5.32 (d, *J* = 8.6 Hz, 0.61H, CH conformer A), *5.12 (d, J = 9.0 Hz, 0.39H, CH conformer B)*, 3.59−3.48 (m, 1H, CH_2 conformer A/B), 3.34−3.19 (m, 1H, CH_2 conformer A/B), 1.14 (t, *J* = 7.2 Hz, 1.83H, CH_3 conformer A), *1.13 (t, J = 7.2 Hz, 1.17H, CH_3 conformer B)*. ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 201.2, 201.1, 184.9, 184.8, 172.8, 172.5, 172.2, 172.1, 171.1, 165.1, 163.2, 150.9, 150.7, 133.6, 133.1, 132.7 (Cq conformer A/B), 60.8 (CH conformer A), *59.9 (CH conformer B)*, 52.6 (CH conformer A), *51.3 (CH conformer B)*, 48.8 (CH_2 conformer A), *48.7 (CH_2 conformer B)*, 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m*/*z* (%) 421 (M$^+$ + 1, 28), 391 (18), 323 (34). HRMS (LSIMS): *m*/*z* 419.8860; calcd for $C_{12}H_8N_2O_3S_6^+$, 419.8859. Anal. Calcd for $C_{12}H_8N_2O_3S_6$: C 34.27, H 1.92, N 6.66. Found: C 34.15, H 2.01, N 6.51.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-methyldihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3b). 52 mg (77%), orange solid, mp 88−89 °C (dec.) (DCM/EtOAc 98:2), 57/43 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 2923, 1783, 1704, 1677, 1639, 1614 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 5.13 (d, *J* = 8.4 Hz, 0.57H, CH conformer A), *5.05 (d, J = 9.2 Hz, 0.43H, CH conformer B)*, 4.88 (d, *J* = 8.4 Hz, 0.57H, CH conformer A), *4.63 (d, J = 9.2 Hz, 0.43H, CH conformer B)*, 3.63−3.48 (m, 1H, CH_2 conformer A/B), 3.29−3.14 (m, 1H, CH_2 conformer A/B), *3.11 (s, 1.29H, CH $_3$ conformer B)*, 3.05 (s, 1.71H, CH_3 conformer A), 1.13 (t, *J* = 7.2 Hz, 3H, CH_3 conformer A/B). ^{13}C NMR and DEPT ($CDCl_3$, 100 MHz): *δ* 201.1, 200.7, 184.7, 184.5, 172.9, 172.6, 172.2, 172.1, 171.1, 165.2, 163.0, 151.1, 150.2, 133.4, 133.3, 132.5 (Cq conformer A/B), 59.7 (CH conformer A), *58.6 (CH conformer B)*, 51.3 (CH conformer A), *50.1 (CH conformer B)*, 48.7 (CH_2 conformer A), *48.6 (CH_2 conformer B)*, *26.1 (CH_3 conformer B)*, 26.0 (CH_3 conformer A), 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m*/*z* (%) 434 (M$^+$, 9), 391 (11), 323 (11). HRMS (LSIMS): *m*/*z* 433.9016; calcd for $C_{13}H_{10}N_2O_3S_6^+$, 433.9016. Anal. Calcd for $C_{13}H_{10}N_2O_3S_6$: C 35.92, H 2.32, N 6.45. Found: C 35.98, H 2.36, N 6.39.

(3a*R*,6a*S*)(*Z*/*E*)-5-(*tert*-Butyl)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3c). 60 mg (81%), orange solid, mp 94−95 °C (dec.) (DCM), 52/48 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 2922, 1704, 1667, 1658, 1642, 1632, 1310, 1190 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 4.98 (d, *J* = 8.8 Hz, 0.52H, CH conformer A), *4.85 (d, J = 9.0 Hz, 0.48H, CH conformer B)*, 4.73 (d, *J* = 8.8 Hz, 0.52H, CH conformer A), *4.44 (d, J = 9.0 Hz, 0.48H, CH conformer B)*, 3.63−3.52 (m, 1H, CH_2 conformer A/B), 3.30−3.19 (m, 1H, CH_2 conformer A/B), 1.62 (s, 4.68H, CH_3 conformer A), *1.58 (s, 4.32H, CH_3 conformer B)*, *1.15 (t, J = 7.2 Hz, 1.44H, CH_3 conformer B)*, 1.14 (t, *J* = 7.2 Hz, 1.56H, CH_3 conformer A). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 200.7, 200.6, 184.7, 184.5, 173.5, 173.3, 172.8, 172.7, 165.6, 164.1, 151.0, 150.3, 133.4, 133.1, 132.5, 130.9, 60.4 (Cq conformer A/B), 60.2 (CH conformer A), *58.7 (CH conformer B)*, 51.8 (CH conformer A), *50.4 (CH conformer B)*, 48.7 (CH_2 conformer A), *48.6 (CH_2 conformer B)* *29.7 (3 × CH_3 conformer B)*, 28.1 (3 × CH_3 conformer A), 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m*/*z* (%) 477 (M$^+$ + 1, 6), 391 (15), 323 (11). HRMS (LSIMS): *m*/*z* 475.9485; calcd for $C_{16}H_{16}N_2O_3S_6^+$, 475.9482. Anal. Calcd for $C_{16}H_{16}N_2O_3S_6$: C 40.32, H 3.38, N 5.88. Found: C 40.26, H 3.46, N 5.92.

(3a*R*,6a*S*)(*Z*/*E*)-5-Butyl-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3d). 65 mg (88%), orange solid, mp 92−93 °C (dec.) (DCM), 52/48 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 2955, 2927, 1782, 1705, 1666, 1639 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 5.11 (d, *J* = 8.6 Hz, 0.52H, CH conformer A), *5.03 (d, J = 8.9 Hz, 0.48H, CH conformer B)*, 4.86 (d, *J* = 8.6 Hz, 0.52H, CH conformer A), 4.62 *(d, J = 8.9 Hz, 0.48H, CH conformer B)*, 3.62−3.48 (m, 3H), 3.28−3.15 (m, 1H, CH_2 conformer A/B), 1.67−1.52 (m, 2H), 1.37−1.24 (m, 2H), *1.13 (t, J = 7.1 Hz, 1.44H, CH $_3$ conformer B)*, 1.12 (t, *J* = 7.1 Hz, 1.56H, CH_3 conformer A), *0.93 (t, J = 7.3 Hz, 1.44H, CH_3 conformer B)*, 0.90 (t, *J* = 7.4 Hz, 1.56H, CH_3 conformer A). ^{13}C NMR and DEPT ($CDCl_3$, 100 MHz): *δ* 200.9, 200.5, 184.7, 184.5, 172.8, 172.5, 172.2, 172.0, 165.3, 163.2, 151.1, 150.3, 133.3, 132.5 (Cq conformer A/B), 59.8 (CH conformer A), *58.6 (CH conformer B)*, 51.31 (CH conformer A), *50.1 (CH conformer B)*, 48.7 (CH_2 conformer A), *48.6 (CH_2 conformer B)*, 39.9, 29.4, 19.9 (CH_2 conformer A/B), *13.5 (CH_3 conformer B)*, 13.4 (CH_3 conformer A), 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m*/*z* (%) 477 (M$^+$ + 1, 4), 338 (10). HRMS (LSIMS): *m*/*z* 475.9502; calcd for $C_{16}H_{16}N_2O_3S_6^+$, 475.9485. Anal. Calcd for $C_{16}H_{16}N_2O_3S_6$: C 40.31, H 3.38, N 5.88. Found: C 40.32, H 3.51, N 5.92.

(3a*R*,6a*S*)(*Z*/*E*)-5-Benzyl-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3e). 41 mg (52%), orange solid, mp 105−106 °C (dec.) (DCM), 52/48 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 2961, 2924, 1783, 1710, 1666, 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.39−7.27 (m, 5H, H_{Ar}), 5.07 (d, *J* = 8.8 Hz, 0.52H, CH conformer A), *4.98 (d, J = 9.0 Hz, 0.48H, CH conformer B)*, 4.82 (d, *J* = 8.8 Hz, 0.52H, CH conformer A), *4.73 (s, 0.96H, CH_2 conformer B)*, 4.66 (s, 1.04H, CH_2 conformer A), *4.55 (d, J = 9.0 Hz, 0.48H, CH conformer B)*, 3.62−3.47 (m, 1H, CH_2 conformer A/B), 3.26−3.14 (m, 1H, CH_2 conformer A/B), 1.13 (t, *J* = 7.0 Hz, 1.56H, CH_3 conformer A), *1.12 (t, J = 7.00 Hz, 1.44H, CH_3 conformer B)*. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 201.1, 200.6, 184.7, 184.5, 172.5, 172.1, 171.8, 171.7, 163.0, 151.0, 150.2, 134.4, 133.4, 132.5 (Cq conformer A/B), 129.0, 128.9, 128.8, 128.8, 128.4 (CH_{Ar}), 59.8 (CH conformer A), *58.7 (CH conformer B)*, 51.3 (CH conformer A), *50.1 (CH conformer B)*, 48.7 (CH_2 conformer A), *48.6 (CH_2 conformer B)*, 43.8 (CH_2 conformer A/B), 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m*/*z* (%) 511 (M$^+$ + 1, 8), 494 (6), 323 (100). HRMS (LSIMS): *m*/*z* 509.9323; calcd for $C_{19}H_{14}N_2O_3S_6^+$, 509.9329. Anal. Calcd for $C_{19}H_{14}N_2O_3S_6$: C 44.69, H 2.76, N 5.49. Found: C 44.58, H 2.84, N 5.38.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-phenyldihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3f). 49 mg (64%), orange solid, mp 119−120 °C (dec.) (DCM/EtOAc 50:50), 53/47 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 2960, 2923, 1783, 1704, 1677, 1666, 1639, 1614, 1536 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.52−7.29 (m, 5H, H_{Ar}), 5.28 (d, *J* = 8.6 Hz, 0.53H, CH conformer A), *5.18 (d, J = 9.0 Hz, 0.47H, CH conformer B)*, 5.03 (d, *J* = 8.6 Hz, 0.53H, CH conformer A), *4.81 (d, J = 9.0 Hz, 0.47H, CH conformer B)*, 3.64−3.49 (m, 1H, CH_2 conformer A/B), 3.32−3.17 (m, 1H, CH_2 conformer A/B), 1.14 (t, *J* = 6.9 Hz, 3H, conformer A/B). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 201.1, 200.6, 184.8, 184.5, 171.9, 171.7, 171.1, 164.9, 162.9 151.2, 150.2, 133.5, 132.4, 130.7 (Cq conformer A/B), 129.3, 129.2, 126.1, 126.0 (CH_{Ar}), 59.9 (CH conformer A), *58.7(CH conformer B)*, 51.5 (CH conformer A), *50.0 (CH conformer B)*, 48.7 (CH_2 conformer A), *48.6 (CH_2 conformer B)*, 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m*/*z* (%) 496 (M$^+$ + 1, 9), 338 (27). HRMS (LSIMS): *m*/*z* 496.9239; calcd for $[C_{18}H_{12}N_2O_3S_6 + H]^+$, 496.9245. Anal. Calcd for $C_{18}H_{12}N_2O_3S_6$: C 43.53, H 2.44, N 5.64. Found: C 43.40, H 2.56, N 5.72.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(4-iodophenyl)-dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3g). 69 mg (72%), orange solid, mp 144−145 °C (dec.) (DCM), 55/45 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3289, 2922, 1716, 1644, 1285, 1163 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.85−7.79 (m, 2H, H_{Ar}), 7.15−7.09 (m, 2H, H_{Ar}), 5.25 (d, *J* = 8.4 Hz, 0.55H, CH conformer A), *5.14 (d, J = 9.0 Hz, 0.45H, CH conformer B)*, 5.00 (d, *J* = 8.4 Hz, 0.55H, CH conformer A), *4.73 (d, J = 9.0 Hz, 0.45H, CH conformer B)*, 3.67−3.53 (m, 1H, CH_2 conformer A/B), 3.33−3.18 (m, 1H, CH_2 conformer A/B), 1.16 (t, *J* = 7.0 Hz, 3H, CH_3 conformer A/B). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 201.3, 201.1, 184.7, 184.5, 171.4, 171.2, 170.6, 170.6, 164.2, 162.3, 151.0,

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150.2 (Cq conformer A/B), 138.6, 138.5 (CH_{Ar}), 132.5, 132.4, 130.6, (Cq), 127.68 (CH_{Ar}), 94.9, 94.8 (Cq conformer A/B), 59.9 (CH conformer A), *58.6 (CH conformer B)*, 51.5 (CH conformer A), *50.4 (CH conformer B)*, 48.9 (CH_2 conformer A), *48.7 (CH_2 conformer B)*, 13.3 (CH_3 conformer A/B). MS (FAB $^+$): *m/z* (%) 623 (M^+ + 1, 10), 410 (10), 340 (52). HRMS (LSIMS): *m/z* 622.8204; calcd for $[C_{18}H_{11}IN_2O_3S_6 + H]^+$, 622.8212. Anal. Calcd for $C_{18}H_{11}IN_2O_3S_6$: C 34.73, H 1.78, N 4.50. Found: C 34.64, H 1.86, N 4.41.

(3a*R*,6a*S*)(*Z*/*E*)-5-(4-Acetylphenyl)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3h). 49 mg (59%), orange solid, mp 139−140 °C (dec.) (DCM/EtOAc 90:10), 55/45 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 2922, 1790, 1721, 1682, 1602, 1558, 1538, 1378, 1263, 1180 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.08−8.01 (m, 2H, H_{Ar}), 7.53−7.44 (m, 2H, H_{Ar}), 5.32 (d, *J* = 8.6 Hz, 0.55H, CH conformer A), *5.21 (d, J = 9.0 Hz, 0.45H, CH conformer B)*, 5.07 (d, *J* = 8.6 Hz, 0.55H, CH conformer A), *4.85 (d, J = 9.0 Hz, 0.45H, CH conformer B)*, 3.65−3.48 (m, 1H, CH_2 conformer A/B), 3.33−3.16 (m, 1H, CH_2 conformer A/B), *2.61 (s, 1.35H, CH $_3$ conformer B)*, 2.60 (s, 1.65H, CH_3 conformer A), *1.14 (t, J = 7.2 Hz, 1.35H, CH_3 conformer B)*, 1.13 (t, *J* = 7.1 Hz, 1.65H, CH_3 conformer A/B). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.2, 200.9, 196.8, 184.8, 171.5, 171.3, 170.7, 170.6, 168.9, 164.3, 162.4, 151.1, 150.2, 137.1, 137.0, 134.8, 134.7, 134.4, 133.6, 132.4 (Cq conformer A/B), 129.2, 129.1, 126.0, 125.3 (CH_{Ar}), 60.0 (CH conformer A), *58.6 (CH conformer B)*, 51.5 (CH conformer A), *50.4 (CH conformer B)*, 48.8 (CH_2 conformer A), *48.7 (CH_2 conformer B)*, 26.7 (CH_3 conformer A), *26.6 (CH_3 conformer B)*, 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m/z* (%) 539 (M^+ + 1, 10), 215 (100). HRMS (LSIMS): *m/z* 537.9283; calcd for $C_{20}H_{14}N_2O_4S_6^+$, 537.9278. Anal. Calcd for $C_{20}H_{14}N_2O_4S_6$: C 44.59, H 2.62, N 5.20. Found: C 44.67, H 2.55, N 5.14.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo[4,5-*c*]pyrrole-5-carboxamide (3i). 27 mg (38%), orange solid, mp 114−115 °C (dec.) (EtOAc), 58/42 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3432, 2923, 1790, 1716, 1635, 1261, 1096 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.59 (br s, 2H, NH_2), 5.15 (d, *J* = 8.5 Hz, 0.58H, CH conformer A), *5.05 (d, J = 8.9 Hz, 0.42H, CH conformer B)*, 4.90 (d, *J* = 8.5 Hz, 0.58H, CH conformer A), *4.66 (d, J = 8.9 Hz, 0.42H, CH conformer B)*, 3.64−3.51 (m, 1H, CH_2 conformer A/B), 3.31−3.16 (m, 1H, CH_2 conformer A/B), *1.15 (t, J = 6.9 Hz, 1.26H, CH_3 conformer B)*, 1.14 (t, *J* = 6.9 Hz, 1.74H, CH_3 conformer A). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.3, 200.9, 184.8, 172.3, 171.5, 171.4, 151.1, 150.4, 133.6, 132.5, 125.0 (Cq conformer A/B), 60.7 (CH conformer A), *59.7 (CH conformer B)*, 52.5 (CH conformer A), *51.2 (CH conformer B)*, 48.8 (CH_2 conformer A), *48.7 (CH_2 conformer B)*, 13.3 (CH_3 conformer A), *13.2 (CH_3 conformer B)*. MS (FAB$^+$): *m/z* (%) 464 (M^+ + 1, 20), 391 (100), 340 (55), 177 (82). HRMS (LSIMS): *m/z* 463.8984; calcd for $[C_{13}H_9N_3O_4S_6 + H]^+$, 463.8991. Anal. Calcd for $C_{13}H_9N_3O_4S_6$: C 33.68, H 1.96, N 9.06. Found: C 33.56, H 2.08, N 8.97.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(4-((*E*)-phenyldiazenyl)phenyl)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (3j). 47 mg (51%), orange solid, mp 175−176 °C (dec.) (EtOAc/MeOH 95:5), 55/45 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3010, 2957, 1789, 1718, 1667, 1380, 1189 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.05−7.99 (m, 2H, H_{Ar}), 7.94−7.91 (m, 2H, H_{Ar}), 7.55−7.50 (m, 5H, H_{Ar}), 5.32 (d, *J* = 8.6 Hz, 0.55H, CH conformer A), *5.22 (d, J = 9.0 Hz, 0.45H, CH conformer B)*, 5.06 (d, *J* = 8.6 Hz, 0.55H, CH conformer A), *4.85 (d, J = 9.0 Hz, 0.45H, CH conformer B)*, 3.66−3.51 (m, 1H, CH_2 conformer A/B), 3.35−3.18 (m, 1H, CH_2 conformer A/B), *1.16 (t, J = 7.1 Hz, 1.35H, CH_3 conformer B)*, 1.15 (t, *J* = 7.1 Hz, 1.65H, CH_3 conformer A). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.2, 200.8, 184.8, 184.6, 171.7, 171.5, 165.9, 163.8, 152.4, 152.2, 152.1, 150.2, 133.6, 132.7, 132.6, 132.4 (Cq conformer A/B), 131.5, 129.1, 126.7, 123.6, 123.5, 123.0 (CH_{Ar}), 60.0 (CH conformer A), *58.6 (CH conformer B)*, 51.5 (CH conformer A), *50.5 (CH conformer B)*, 48.8 (CH_2 conformer A), *48.7 (CH_2 conformer B)*, 13.3 (CH_3 conformer A/B). MS (FAB$^+$): *m/z* (%) 601 (M^+ + 1, 10), 600 (M^+, 10). HRMS (LSIMS): *m/z* 600.9616; calcd for $[C_{24}H_{16}N_4O_3S_6 + H]^+$, 600.9625. Anal. Calcd for $C_{24}H_{16}N_4O_3S_6$: C 47.98, H 2.68, N 9.33. Found: C 48.11, H 2.73, N 9.22.

General Procedure for the Catalytic Cycloaddition of 4-Benzylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione (5) and Maleimides 2a−c,e−g. Maleimide **2a**−**c**,**e**−**g** (1 equiv) and $Sc(OTf)_3$ (19 mg, 0.039 mmol) were added under nitrogen to **5** (60 mg, 0.16 mmol) dissolved in dry dichloromethane (10 mL), and the mixture was refluxed for 2 h (for **2a**,**c**), 3 h (for **2b**,**e**,**f**), or 4 h (for **2g**). Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography [silica 230−400 mesh, eluting with light petroleum to dichoromethane (or a dichloromethane/ethyl acetate 95:5 mixture for **6a**,**g**)] to get **6a**−**c**,**e**−**g**. Analytical samples were obtained by thin-layer chromatography (glass plates, silica 20 cm × 20 cm × 0.1 cm, eluting with dichloromethane or dichloromethane/ethyl acetate mixtures).

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Benzyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (6a). 50 mg (67%), orange solid, mp 142−144 °C (dec.) (DCM/EtOAc 95:5), 66/34 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3435, 1790, 1715, 1648, 1264 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.22 (br s, 1H, NH), 7.33−7.19 (m, 3H, H_{Ar}), 7.06−7.04 (m, 2H, H_{Ar}), 5.18 (d, *J* = 8.5 Hz, 0.66H, CH conformer A), *5.08 (d, J = 9.0 Hz, 0.34H, CH conformer B)*, 4.94 (d, *J* = 8.5 Hz, 0.66H, CH conformer A), *4.57 (d, J = 9.0 Hz, 0.34H, CH conformer B)*, 4.52 (d, *J* = 14.2 Hz, 0.66H, CH_2 conformer A), *4.49 (d, J = 13.6 Hz, 0.34H, CH_2 conformer B)*, 4.20−4.08 (m, 1H, CH_2 conformer A/B). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.9, 200.4, 184.8, 184.7, 173.2, 172.8, 172.6, 172.4, 165.0, 162.8, 151.9, 151.4 (Cq conformer A/B), 135.2, 135.1 (CH_{Ar} conformer A/B), 133.2, 133.1, 132.9, 131.7, 131.6 (Cq conformer A/B), 129.6, 129.5, 128.5, 128.4 (CH_{Ar} conformer A/B), 127.9, 127.5 (Cq conformer A/B), 61.0 (CH conformer A), *60.0 (CH conformer B)*, 57.4 (CH_2), 52.7 (CH conformer A), *51.4 (CH conformer B)*. MS (FAB$^+$): *m/z* (%) 483 (M^+ + 1, 6), 391 (20), 274 (60). HRMS (LSIMS): *m/z* 482.9096; calcd for $[C_{17}H_{10}N_2O_3S_6 + H]^+$, 482.9089. Anal. Calcd for $C_{17}H_{10}N_2O_3S_6$: C 42.31, H 2.09, N 5.80. Found: C 42.22, H 2.21, N 5.69.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Benzyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-methyldihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (6b). 54 mg (70%), orange solid, mp 200−203 °C (dec.) (DCM). IR (KBr): $\tilde{\nu}$ = 1706, 1660, 1432, 1283 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32−7.04 (m, 5H, H_{Ar}), 5.15 (d, *J* = 8.6 Hz, 0.59H, CH conformer A), *5.07 (d, J = 9.0 Hz, 0.41H, CH conformer B)*, 4.92 (d, *J* = 8.6 Hz, 0.59H, CH conformer A), *4.67 (d, J = 9.0 Hz, 0.41H, CH conformer B)*, 4.56 (d, *J* = 14.3 Hz, 0.59H, CH_2 conformer A), *4.50 (d, J = 14.7 Hz, 0.41H, CH_2 conformer B)*, 4.17−4.12 (m, 1H, CH_2 conformer A/B), *3.15 (s, 1.23H, CH_3 conformer B)*, 3.06 (s, 1.77H, CH_3 conformer A). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.0, 200.6, 184.5, 184.3, 172.9, 172.5, 172.2, 172.1, 171.1, 164.8, 162.4, 151.8, 150.9 (Cq conformer A/B), 135.1, 135.2 (CH_{Ar} conformer A/B), 133.1, 132.9, 131.6 (Cq conformer A/B), 129.6, 129.5, 128.5, 128.4 (CH_{Ar} conformer A/B), 59.8 (CH conformer A), *58.7 (CH conformer B)*, *57.4 (CH_2 conformer B)*, 57.3 (CH_2 conformer A), 51.4 (CH conformer A), *50.3 (CH conformer B)*, *26.1 (CH_3 conformer B)*, 25.9 (CH_3 conformer A). MS (FAB$^+$): *m/z* (%) 497 (M^+ + 1, 10), 464 (15), 405 (60), 301 (100). HRMS (LSIMS): *m/z* 495.9181; calcd for $C_{18}H_{12}N_2O_3S_6^+$, 495.9172. Anal. Calcd for $C_{18}H_{12}N_2O_3S_6$: C 43.53, H 2.44, N 5.64. Found: C 43.64, H 2.35, N 5.52.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Benzyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(*tert*-butyl)-dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (6c). 62 mg (74%), orange solid, mp 185−186 °C (dec.) (DCM), 55/45 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1706, 1650, 1331, 1159 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.31−7.04 (m, 5H, H_{Ar}), 5.02 (d, *J* = 8.8 Hz, 0.55H, conformer A), *4.89 (d, J = 9.1 Hz, 0.45H, conformer B)*, 4.79 (d, *J* = 8.8 Hz, 0.55H, conformer A), 4.58−4.49 (m, 1.45H, CH conformer B and CH_2 conformer A/B), 4.20−4.11 (m, 1H, CH_2 conformer A/B), *1.64 (s, 4.05H, $(CH_3)_3$ conformer B)*, 1.58 (s, 4.95 H $(CH_3)_3$ conformer A). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.6, 200.2, 184.4, 184.1, 172.9, 172.5, 172.3, 172.4, 164.7, 162.4, 151.5, 151.0 (Cq conformer A/B), 135.0, 134.8 (CH_{Ar} conformer A/B), 132.8, 132.7, 132.5, 131.3, 131.2 (Cq conformer A/B), 129.2, 129.0, 128.1, 127.9 (CH_{Ar} conformer A/

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B), 127.4, 127.1 (Cq conformer A/B), 60.5 (CH conformer A), 60.4 (Cq conformer A/B), *59.9 (CH conformer B)*, 58.5 (CH_2), 52.3 (CH conformer A), *51.0 (CH conformer B)*, *29.7 (3 × CH_3 conformer B)*, 28.1 (3 × CH_3 conformer A). MS (FAB^+): *m/z* (%) 539 (M^+ + 1, 30), 447 (70), 391 (70), 349 (90). HRMS (LSIMS): *m/z* 537.9635; calcd for $C_{21}H_{18}N_2O_3S_6^+$, 537.9642. Anal. Calcd for $C_{21}H_{18}N_2O_3S_6$: C 46.82, H 3.37, N 5.20. Found: C 46.69, H 3.46, N 5.12.

(3a*R*,6a*S*)(*Z*/*E*)-5-Benzyl-2-(4-benzyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (6e). 59 mg (66%), orange solid, mp 116−117 °C (dec.) (DCM), 62/38 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3024, 2924, 1709, 1649, 1387, 1276, 1064 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.43−7.20 (m, 8H, H_{Ar}), 7.06−7.01 (m, 2H, H_{Ar}), 5.11 (d, *J* = 8.6 Hz, 0.62H, CH conformer A), *5.02 (d, J = 9.0 Hz, 0.38H, CH conformer B)*, 4.91 (d, *J* = 8.6 Hz, 0.62H, CH conformer A), *4.77 (s, 0.76H, CH_2 conformer B)*, 4.67 (s, 1.24H, CH_2 conformer A), *4.64 (d, J = 9.0 Hz, 0.38H, CH conformer B)*, 4.59 (d, *J* = 14.3 Hz, 0.62H, CH_2 conformer A), *4.52 (d, J = 14.2 Hz, 0.38H, CH_2 conformer B)*, *4.12 (d, J = 14.2 Hz, 0.38H, CH_2 conformer B)*, 4.11 (d, *J* = 14.3 Hz, 0.62H, CH_2 conformer A). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.1, 200.6, 184.5, 184.4, 172.5, 172.1, 171.9, 171.8, 164.5, 162.4, 151.7, 150.9, 135.3, 135.1, 134.5, 134.4, 133.1, 132.9, 131.7, 131.6 (Cq conformer A/B), 129.6, 129.5, 129.1, 128.9, 128.8, 128.5, 128.4 (CH_{Ar} conformer A/B), 59.9 (CH conformer A), *58.8 (CH conformer B)*, 57.4 (CH_2 conformer A/B), 51.4 (CH conformer A), *50.2 (CH conformer B)*, 43.7 (CH_2 conformer A/B). MS (FAB^+): *m/z* (%) 573 (M^+ + 1, 50), 481 (100), 386 (85), 296 (69), 214 (71). HRMS (LSIMS): *m/z* 572.9564; calcd for $[C_{24}H_{16}N_2O_3S_6 + H]^+$, 572.9558. Anal. Calcd for $C_{24}H_{16}N_2O_3S_6$: C 50.33, H 2.82, N 4.89. Found: C 50.41, H 2.75, N 4.83.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Benzyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-phenyldihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (6f). 44 mg (51%), orange solid, mp 210−211 °C (dec.) (DCM), 65/35 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3024, 1705, 1654, 1623, 1383, 1184 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 7.56−6.99 (m, 10H, H_{Ar}), 5.83 (d, *J* = 8.9 Hz, 0.65H, CH conformer A), *5.66 (d, J = 9.2 Hz, 0.35H, CH conformer B)*, 5.58 (d, *J* = 8.9 Hz, 0.65H, CH conformer A), *5.35 (d, J = 9.2 Hz, 0.35H, CH conformer B)*, 4.40 (d, *J* = 14.4 Hz, 0.65H, CH_2 conformer A), *4.37 (d, J = 14.1 Hz, 0.35H, CH_2 conformer B)* *4.19 (d, J = 14.1 Hz, 0.35H, CH_2 conformer B)*, 4.12 (d, *J* = 14.4 Hz, 0.65H, CH_2 conformer A). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 200.6, 199.9, 184.9, 173.1, 172.8, 172.6, 168.4, 166.6, 152.0, 151.7, 135.5, 132.0, 131.7, 131.6, 131.5 (Cq conformer A/B), 129.4, 129.3, 129.1, 129.0, 128.9, 128.3, 128.2, 127.0, 126.9 (CH_{Ar}), 60.7 (CH conformer A), *59.5 (CH conformer B)*, 56.6 (CH_2 conformer A), *56.5 (CH_2 conformer B)*, 51.8 (CH conformer A), *50.6 (CH conformer B)*. MS (FAB^+): *m/z* (%) 559 (M^+ + 1, 15), 467 (62), 386 (50), 295 (40), 237 (100). HRMS (LSIMS): *m/z* 557.9322; calcd for $C_{23}H_{14}N_2O_3S_6^+$, 557.9329. Anal. Calcd for $C_{23}H_{14}N_2O_3S_6$: C 49.44, H 2.53, N 5.01. Found: C 49.33, H 2.61, N 4.92.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Benzyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(4-iodophenyl)-dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (6g). 51 mg (48%), orange solid, mp 155−156 °C (dec.) (DCM/EtOAc 95:5), 55/45 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3022, 1707, 1654, 1380, 1182 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.87−7.77 (m, 2H, H_{Ar}), 7.37−7.05 (m, 7H, H_{Ar}), 5.31 (d, *J* = 8.4 Hz, 0.55H, CH conformer A), *5.19 (d, J = 8.9 Hz, 0.45H, CH conformer B)*, 5.08 (d, *J* = 8.4 Hz, 0.55H, CH conformer A), *4.83 (d, J = 8.9 Hz, 0.45H, CH conformer B)*, 4.58 (d, *J* = 14.2 Hz, 0.55H, CH_2 conformer A), *4.54 (d, J = 14.2 Hz, 0.45H, CH_2 conformer B)*, *4.19 (d, J = 14.2 Hz, 0.45H, CH_2 conformer B)*, 4.15 (d, *J* = 14.2 Hz, 0.55H, CH_2 conformer A). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.3, 201.0, 184.4, 171.4, 171.1, 170.6, 170.5, 151.7, 150.8 (Cq conformer A/B), 138.6, 138.5 (CH_{Ar} conformer A/B), 135.2, 135.0, 133.4, 131.6 (Cq conformer A/B), 129.7, 129.6, 128.8, 128.5, 127.7, 127.6 (CH_{Ar} conformer A/B), 94.9, 94.8 (Cq conformer A/B), 59.9 (CH conformer A), *58.6 (CH conformer B)*, 57.4 (CH_2), 51.6 (CH conformer A), *50.4 (CH conformer B)*. MS (FAB^+): *m/z* (%) 685 (M^+ + 1, 10), 593 (30), 410 (28), 340 (80), 177 (100). HRMS (LSIMS): *m/z* 684.8374; calcd for $[C_{23}H_{13}IN_2O_3S_6 + H]^+$, 684.8368. Anal. Calcd for $C_{23}H_{13}IN_2O_3S_6$: C 40.35, H 1.91, N 4.09. Found: C 40.44, H 1.83, N, 3.98.

General Procedure for the Catalytic Cycloaddition of 4-Ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3,5-dithione (7) and Maleimides 2b,f,g. Maleimide **2b**,**f**,**g** (2 equiv) and $Sc(OTf)_3$ (37 mg, 0.075 mmol) were added under nitrogen to **7** (50 mg, 0.15 mmol) dissolved in dry dichloromethane (10 mL), and the mixture was refluxed for 1 h (for **2b**,**g**) or 2 h (for **2c**). Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography [silica 230−400 mesh, eluting with light petroleum to dichloromethane/ethyl acetate mixtures (95:5 for **8b**,**g**, 90:10 for **8f**)] to get **8b**,**f**,**g**. Analytical samples were obtained by thin-layer chromatography (glass plates, silica 20 cm × 20 cm × 0.1 cm, eluting with dichloromethane/ethyl acetate mixtures).

(2*Z*/*E*,2′*E*/*Z*,3a*R*,3a′*R*,6a*S*,6a′*S*)-2,2′-(4-Ethyl-2,6-dithioxothiomorpholine-3,5-diylidene)bis(5-methyldihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione) (8b). 54 mg (65%), light-brown solid, mp 144−145 °C (dec.) (DCM/EtOAc 95:5), 60/24/13/3 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1708, 1650, 1420, 1365 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 5.66−5.51 (m, 2H, 2 × CH conformer A/B/C), 5.36−5.22 (m, 2H, 2 × CH conformer A/B/C), 3.30−3.20 (m, 2H, CH_2), *2.95 (s, 1.49H, 2 × CH_3 conformer B)*, 2.94 (s, 1.83H, CH_3 conformer A), 2.90 (s, 1.83H, CH_3 conformer A), *2.89 (s, 0.85H, 2 × CH_3 conformer C)*, 1.14−1.03 (m, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 201.1, 199.8, 199.7, 198.4, 173.9, 173.8, 173.6, 173.5, 173.4, 173.3, 173.1, 172.0, 171.9, 171.3, 170.8, 135.0, 134.3, 134.0, 133.2 (Cq conformer A/B/C), 60.4, 60.3, 59.8, 59.6, 51.0, 50.9, 50.4 (CH conformer A/B/C), 50.3 (CH_2), 50.0 (CH conformer A/B/C), 25.6, 25.5, 25.4 (CH_3 conformer A/B/C), 13.0, 12.9 (CH_3 conformer A/B/C). MS (FAB^+): *m/z* (%) 562 (M^+ + 1, 12), 392 (30), 281 (36), 167 (100). HRMS (LSIMS): *m/z* 561.9175; calcd for $[C_{18}H_{15}N_3O_4S_7 + H]^+$, 561.9181. Anal. Calcd for $C_{18}H_{15}N_3O_4S_7$: C 38.49, H 2.69, N 7.48. Found: C 38.36, H 2.77, N 7.40.

(2*Z*/*E*,2′*E*/*Z*,3a*R*,3a′*R*,6a*S*,6a′*S*)-2,2′-(4-Ethyl-2,6-dithioxothiomorpholine-3,5-diylidene)bis(5-phenyldihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione) (8f). 68 mg (67%), light-brown solid, mp 104−105 °C (dec.) (DCM/EtOAc 90:10), 45/45/7/3 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1717, 1633, 1378 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ (for the main conformer) 7.52−7.33 (m, 10H, H_{Ar}), 5.81 (d, *J* = 8.8 Hz, 1H, CH), 5.68 (d, *J* = 9.0 Hz, 1H, CH), 5.54 (d, *J* = 8.8 Hz, 1H, CH), 4.45 (d, *J* = 9.0 Hz, 1H, CH), 3.35 (q, *J* = 7.0 Hz, 2H, CH_2), 1.12 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (for the main conformer) 201.0, 198.7, 173.0, 172.9, 172.6, 172.5, 172.1, 171.0, 135.0, 133.6 (Cq), 131.6, 131.5, 129.2, 129.1, 127.0, 126.9 (CH_{Ar}), 60.7, 60.1, 51.5, 50.7 (CH), 50.5 (CH_2), 13.0 (CH_3). MS (FAB^+): *m/z* (%) 686 (M^+ + 1, 40), 513 (58). HRMS (LSIMS): *m/z* 685.9485; calcd for $[C_{28}H_{19}N_3O_4S_7 + H]^+$, 685.9494. Anal. Calcd for $C_{28}H_{19}N_3O_4S_7$: C 49.03, H 2.79, N 6.13. Found: C, 49.12, H 2.68, N 6.05.

(2*Z*/*E*,2′*E*/*Z*,3a*R*,3a′*R*,6a*S*,6a′*S*)-2,2′-(4-Ethyl-2,6-dithioxothiomorpholine-3,5-diylidene)bis(5-(4-iodophenyl)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione) (8g). 21 mg (15%), light-brown solid, mp 184−185 °C (dec.) (DCM/EtOAc 95:5), 75/12/11/2 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1710, 1640, 1375 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ (for the main conformer) 7.92−7.85 (m, 2H, H_{Ar}), 7.70−7.65 (m, 2H, H_{Ar}), 7.21−7.17 (m, 2H, H_{Ar}), 7.10−7.07 (m, 2H, H_{Ar}), 5.78 (d, *J* = 8.7 Hz, 2H, 2 × CH), 5.47 (d, *J* = 8.7 Hz, 2H, 2 × CH), 3.32 (q, *J* = 7.2 Hz, 2H, CH_2), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (for the main conformer) 199.9, 172.7, 172.2, 172.0 (Cq), 137.8 (CH_{Ar}), 134.4, 131.1 (Cq), 129.0 (CH_{Ar}), 95.2 (Cq), 60.5 (CH), 51.5 (CH), 34.31 (CH_2), 13.0 (CH_3). MS (FAB^+): *m/z* (%) 938 (M^+ + 1, 1). Anal. Calcd for $C_{28}H_{17}I_2N_3O_4S_7$: C 35.87, H 1.83, N 4.48. Found: C 35.96, H 1.75, N 4.36.

General Procedure for the Catalytic Cycloaddition of 4-Ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione 1 and Bismaleimides 9a−c. Bismaleimide **9a**−**c** (1 equiv) and $Sc(OTf)_3$ (19 mg, 0.038 mmol or 37 mg, 0.075 mmol) were added under nitrogen to 1 equiv (50 mg, 0.15 mmol, method A) or 2 equiv (100 mg, 0.30 mmol, method B) of **1** dissolved in dry dichloromethane (10 mL), and the mixture was refluxed for 1 h. Then the solvent was evaporated under reduced pressure, and the residue was purified by

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column chromatography (silica 230−400 mesh, eluting with light petroleum/dichloromethane 60:40 to dichloromethane/ethyl acetate 90:10) to get **10a−b** and **11a−c**. Analytical samples were obtained by thin-layer chromatography (glass plates, silica 20 cm × 20 cm × 0.1 cm, eluting with dichloromethane/ethyl acetate mixtures).

(3a*R*,6a*S*)(*Z*/*E*)-5-(4-(4-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)benzyl)phenyl)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (10a). 59 mg (56%) by method A or 26 mg (25%) by method B, orange solid, mp 285−286 °C (dec.) (DCM/EtOAc 90:10), 53/47 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1788, 1712, 1666, 1639, 1536, 1376 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.21 (m, 8H, H_{Ar}), *6.83 (s, 0.94H, CH_{vin} conformer B)*, 6.82 (s, 1.06H, CH_{vin} conformer A), 5.24 (d, *J* = 8.4 Hz, 0.53H, CH conformer A), *5.12 (d, J = 9.2 Hz, 0.47H, CH conformer B)*, 4.98 (d, *J* = 8.4 Hz, 0.53H, CH conformer A), *4.74 (d, J = 9.2 Hz, 0.47H, CH conformer B)*, *4.04 (s, 0.94H, CH_2 conformer B)*, 4.01 (s, 1.06H, CH_2 conformer A), 3.63−3.49 (m, 1H, CH_2 conformer A/B), 3.31−3.16 (m, 1H, CH_2 conformer A/B), 1.13 (t, *J* = 7.2 Hz, 1.59H, CH_3 conformer A), *1.12 (t, J= 7.2 Hz, 1.41H, CH_3 conformer B)*. ^{13}C NMR and DEPT ($CDCl_3$, 100 MHz): δ 201.1, 200.7, 184.7, 184.5, 171.8, 171.7, 171.1, 169.5, 165.0, 162.9, 151.1, 150.2, 141.8, 141.7, 140.0 (Cq conformer A/B), 134.2 (CH conformer A/B), 133.5, 133.4, 132.4 (Cq conformer A/B), 129.8, 129.7, 129.6 (CH conformer A/B), 129.4, 126.3, 129.0, 128.9 (Cq conformer A/B), 126.2, 126.1 (CH conformer A/B), 59.9, 58.6, 51.5, 50.4 (CH conformer A/B), 48.8, 48.6 (CH_2 conformer A/B), 41.1, 41.0 (CH_2 conformer A/B), 13.3, 13.2 (CH_3 conformer A/B). MS (FAB^+): *m*/*z* (%) 684 (M^+ + 2, 9), 487 (22), 391 (45). HRMS (LSIMS): *m*/*z* 682.9813; calcd for $[C_{29}H_{19}N_3O_5S_6 + 2H]^+$, 682.9805. Anal. Calcd for $C_{29}H_{19}N_3O_5S_6$: C 51.08, H 2.81, N 6.16. Found: C 51.21, H 2.90, N 6.17.

(3a*R*,6a*S*)(*Z*/*E*)-5-(4-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-phenyl)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*]-[1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]-pyrrole-4,6(5*H*)-dione (10b). 25 mg (27%) by method A or 24 mg (26%) by method B, orange solid, mp >300 °C (dec.) (DCM/EtOAc 90:10), 55/45 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1789, 1715, 1666, 1634, 1536, 1367 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.57−7.42 (m, 4H, H_{Ar}), *6.88 (s, 0.9H, CH_{vin} conformer B)*, 6.86 (s, 1.1H, CH_{vin} conformer A), 5.29 (d, *J* = 8.6 Hz, 0.55H, CH conformer A), *5.18 (d, J = 8.9 Hz, 0.45H, CH conformer B)*, 5.04 (d, *J* = 8.6 Hz, 0.55H, CH conformer A), *4.79 (d, J = 8.9 Hz, 0.45H, CH conformer B)*, 3.70−3.47 (m, 1H, CH_2 conformer A/B), 3.37−3.13 (m, 1H, CH_2 conformer A/B), 1.15 (t, *J* = 7.1 Hz, 3H, CH_3 conformer A/B). ^{13}C NMR and DEPT ($CDCl_3$, 50 MHz): δ 201.4, 176.5, 171.9, 169.0 (Cq conformer A/B), 134.3 (CH conformer A/B), 132.5 (Cq conformer A/B), 126.9, 126.8, 126.7, 126.3 (CH conformer A/B), 59.9, 58.6, 51.5, 50.4 (CH conformer A/B), 48.8, 48.7 (CH_2 conformer A/B), 13.3 (CH_3 conformer A/B). MS (FAB^+): *m*/*z* (%) 593 (M^+ + 2, 1). Anal. Calcd for $C_{22}H_{13}N_3O_5S_6$: C 44.65, H 2.21, N 7.10. Found: C 44.51, H 2.28, N 7.03.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(4-(4-((3a*R*,6a*S*)(*E*/*Z*)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]-thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo-[4,5-*c*]pyrrol-5-yl)benzyl)phenyl)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (11a). 10 mg (13%) by method A or 86 mg (55%) by method B, orange solid, mp 179−180 °C (dec.) (DCM/EtOAc 90:10), 25/28/23/24 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 1788, 1719, 1665, 1657, 1633, 1510, 1376 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31−7.20 (m, 8H, H_{Ar}), 5.25 (d, *J* = 8.6 Hz, 0.50H, conformer A), *5.24 (d, J = 8.6 Hz, 0.52H, conformer B)*, *5.14 (d, J = 9.0 Hz, 0.48H, conformer C)*, *5.13 (d, J = 8.9 Hz, 0.50H, conformer D)*, 4.99 (d, *J* = 8.6 Hz, 0.50H, conformer A), *4.98 (d, J = 8.6 Hz, 0.52H, conformer B)*, *4.74 (d, J = 9.0 Hz, 0.48H, conformer C)*, *4.73 (d, J = 8.9 Hz, 0.50H, conformer D)*, 4.04 (d, *J* = 10.5 Hz, 1H, CH_2), 4.01 (d, *J* = 10.5 Hz, 1H, CH_2), 3.64−3.49 (m, 2H), 3.32−3.17 (m, 2H), 1.14 (t, *J* = 7.0 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.5, 201.1, 200.1, 185.0, 184.8, 172.1, 172.0, 171.9, 171.4, 171.3, 171.2, 165.0, 163.0, 151.3, 150.4, 141.8, 141.7, 141.6, 133.8, 133.7, 132.7 (Cq conformers A/B/C/D), 130.2, 130.1, 130.0 (CH_{Ar}), 129.4, 129.3, 129.2 (Cq conformers A/B/C/D), 126.5, 126.4 (CH_{Ar}), 60.2, 58.9, 51.8, 50.6 (CH conformers A/B/C/D), 49.0, 48.9 (CH_2 conformers A/B/C/D), 41.3 (CH_2), 13.6 (CH_3 conformers A/B/C/D). MS (FAB^+): *m*/*z* (%) 1006 (M^+ + 2, 14), 880 (15), 599 (32). HRMS (LSIMS): *m*/*z* 1005.8487; calcd for $[C_{37}H_{24}N_4O_6S_{12} + 2H]^+$, 1005.8501. Anal. Calcd for $C_{37}H_{24}N_4O_6S_{12}$: C 44.20, H 2.41, N 5.57. Found: C 44.14, H 2.35, N 5.45.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(4-((3a*R*,6a*S*)(*E*/*Z*)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]-thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo-[4,5-*c*]pyrrol-5-yl)phenyl)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]-pyrrole-4,6(5*H*)-dione (11b). 24 mg (17%) by method A or 34 mg (24%) by method B, orange solid, mp 214−215 °C (dec.) (DCM/EtOAc 90:10), mixture of conformers. IR (KBr): $\tilde{\nu}$ = 1788, 1720, 1666, 1633, 1536, 1361 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53−7.46 (m, 4H, H_{Ar}), 5.28−5.25 (m, 1.11H, mixture of conformers), 5.18−5.14 (m, 0.89H, mixture of conformers), 5.04−5.00 (m, 1.11H, mixture of conformers), 4.79−4.75 (m, 0.89H, mixture of conformers), 3.65−3.51 (m, 2H, CH_2), 3.36−3.17 (m, 2H, CH_2), 1.17−1.12 (m, 6H, CH_3). ^{13}C NMR and DEPT ($CDCl_3$, 100 MHz): δ 201.5, 201.4, 184.7, 171.5, 171.3, 171.2, 170.7, 170.6, 150.1, 146.5, 134.3, 133.7, 132.5 (Cq), 126.9 and 126.8 (CH_{Ar}), 59.9, 58.6, 51.5, 50.4 (CH, mixture of conformers), 48.8, 48.7 (CH_2, mixture of conformers), 13.3 (CH_3, mixture of conformers). MS (FAB^+): *m*/*z* (%) 915 (M^+ + 1, 12), 391 (18), 338 (21). HRMS (LSIMS): *m*/*z* 914.7964; calcd for $[C_{30}H_{18}N_4O_6S_{12} + H]^+$, 914.7953. Anal. Calcd for $C_{30}H_{18}N_4O_6S_{12}$: C 39.37, H 1.98, N 6.12. Found: C 39.49, H 1.89, N 6.02.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(2-(2-(2-((3a*R*,6a*S*)-(*E*/*Z*)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]-thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo-[4,5-*c*]pyrrol-5-yl)ethoxy)ethoxy)ethyl)dihydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (11c). 31 mg (21%) by method B, orange solid, mp 145−146 °C (dec) (DCM/EtOAc 90:10), mixture of conformers. IR (KBr): $\tilde{\nu}$ = 1783, 1709, 1651, 1393 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 5.31−4.71 (m, 4H), 3.79 (m, 14H), 3.29−3.18 (m, 2H), 1.18−1.12 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.9, 200.6, 184.5, 173.3, 173.2, 172.4, 163.8, 150.4, 133.4, 132.6, 132.5, 130.9, 128.8, 125.0 (Cq, mixture of conformers), 70.0, 66.7 (CH_2, mixture of conformers), 59.8, 58.8, 51.6, 50.1 (CH, mixture of conformers), 48.8, 48.7, 39.4, 39.2 (CH_2, mixture of conformers), 13.3, 13.2 (CH_3, mixture of conformers). MS (FAB^+): *m*/*z* (%) 956 (M^+ + 2, 1). Anal. Calcd for $C_{30}H_{26}N_4O_8S_{12}$: C 37.72, H 2.74, N 5.87. Found: C 37.85, H 2.84, N 5.74.

(3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]-dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-5-(4-(4-((3a*R*,6a*S*)(*E*/*Z*)-2-((*Z*/*E*)-4-ethyl-5-((3a*R*,6a*S*)-5-(4-(4-((3a*R*,6a*S*)(*E*/*Z*)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo[4,5-*c*]-pyrrol-5-yl)benzyl)phenyl)-4,6-dioxotetrahydro-4*H*-[1,3]-dithiolo[4,5-*c*]pyrrol-2-ylidene)-2,6-dithioxothiomorpholin-3-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo[4,5-*c*]pyrrol-5-yl)benzyl)phenyl)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (12). Maleimide **10a** (60 mg, 0.088 mmol) and $Sc(OTf)_3$ (9 mg, 0.018 mmol) were added under nitrogen to 4-ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3,5-dithione (**7**) (15 mg, 0.044 mmol) dissolved in dry dichloromethane (10 mL), and the mixture was refluxed for 6 hours. Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica 230−400 mesh, eluting with light petroleum to dichoromethane/ethyl acetate 50:50) to get **12** (56 mg, 74% yield). An analytical sample of **12** was obtained by thin-layer chromatography (glass plates, silica 20 cm × 20 cm × 0.1 cm, eluting with dichloromethane/ethyl acetate 50:50). Yellow solid, mp 238−239 °C (dec.) (DCM/EtOAc 50:50). IR (KBr): $\tilde{\nu}$ = 1790, 1715, 1664, 1635, 1537, 1378 cm^{-1}. ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.37−7.19 (m, 16H, H_{Ar}), 5.23−4.78 (m, 8H, 8 × CH), 4.11−4.06 (m, 4H, 2 × CH_2), 3.61−3.49 (m, 3H), 3.31−3.18 (m, 3H), 1.16−1.12 (m, 9H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 201.9, 201,4, 184.8, 172.2, 171.9, 171.6, 171.5, 163.5, 151.3, 150.5, 142.1, 142.0 (Cq), 135.4 (CH_{Ar}), 134.4, 133.8, 133.7, 132.7 (Cq), 130.0, 126.6, 125.2 (CH_{Ar}), 60.3, 59.1, 51.8, 50.7 (CH), 49.0, 48.9, 41.2 (CH_2), 13.3, 13.2 (CH_3). MS (FAB^+): *m*/*z* (%)

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1702 (M^+ + 1, 58), 1552 (70), 1389 (78), 1341 (100). HRMS (LSIMS): m/z 1701.7826; calcd for $[C_{66}H_{43}N_7O_{10}S_{19} + H]^+$, 1701.7838. Anal. Calcd for $C_{66}H_{43}N_7O_{10}S_{19}$: C 46.54, H 2.54, N 5.76. Found: C 46.54, H 2.54, N 5.76.

Catalytic Cycloaddition of 4-Ethylbis[1,2]dithiolo[3,4-*b*:4′,3′-*e*][1,4]thiazin-3-oxo-5-thione (1) and Trismaleimide 13. Trismaleimide **13** (60 mg, 0.15 mmol) and $Sc(OTf)_3$ [19 mg, 0.038 mmol (method A)/37 mg, 0.075 mmol (method B)/56 mg, 0.11 mmol (method C)] were added under nitrogen to **1** [50 mg, 0.15 mmol (method A)/100 mg, 0.30 mmol (method B)/150 mg, 0.45 mmol (method C)] dissolved in dry dichloromethane (10 mL), and the mixture was refluxed for 4 h. Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica 230−400 mesh, eluting with light petroleum to dichloromethane/ethyl acetate 50:50) to get monoadduct **14**, diadduct **15**, or triadduct **16**. Analytical samples were obtained by thin-layer chromatography (glass plates, silica 20 cm × 20 cm × 0.1 cm, eluting with dichloromethane/ethyl acetate mixtures).

1,1′-(((2-((3a*R*,6a*S*)(*Z*/*E*)-2-(4-Ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo[4,5-*c*]pyrrol-5-yl)ethyl)azanediyl)bis(ethane-2,1-diyl))bis(1*H*-pyrrole-2,5-dione) (14). 46 mg (42%) by method A or 15 mg (14%) by method B or 12 mg (11%) by method C, orange solid, mp 255−256 °C (dec.) (DCM/EtOAc 50:50), 57/43 ratio of conformers. IR (KBr): $\tilde{\nu}$ = 3099, 1782, 1711, 1404, 1332 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.65 (s, 4H), 5.33 (d, J = 8.5 Hz, 0.57H, CH adduct A), *5.22 (d, J = 9.0 Hz, 0.43H, CH adduct B)*, 5.03 (d, J = 8.5 Hz, 0.57H, CH adduct A), *4.84 (d, J = 9.0 Hz, 0.43H, CH adduct B)*, 3.59−3.52 (m, 1H), 3.48 (t, J = 6.6 Hz, 4H), 3.41−3.34 (m, 2H), 3.26−3.12 (m, 1H), 2.67 (t, J = 6.6 Hz, 4H), 2.61−2.47 (m, 2H), 1.11−1.08 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.8, 200.3, 185.0, 184.9, 184.7, 173.3, 172.9, 171.0, 170.7, 166.8, 164.6, 151.5, 150.4, 134.3, 134.2, 133.3, 133.2, 132.7, 132.6, 125.1, 60.4, 59.4, 52.7, 51.7, 51.4, 50.6, 48.9, 48.8, 37.9, 35.8, 35.7, 13.5, 13.4. MS (FAB^+): m/z (%) 711 (M^+ + 2, 2). Anal. Calcd for $C_{26}H_{23}N_5O_7S_6$: C 43.99, H 3.27, N 9.87. Found: C 43.86, H 3.38, N 9.78.

(3a*R*,6a*S*)(*Z*/*E*)-5-(2-((2-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)ethyl)(2-((3a*R*,6a*S*)(*E*/*Z*)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6H)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo[4,5-*c*]pyrrol-5-yl)ethyl)amino)ethyl)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione (15). 15 mg (19%) by method A or 61 mg (38%) by method B or 32 mg (20%) by method C, orange solid, mp 240−241 °C (dec.) (DCM/EtOAc 50:50), mixture of conformers. IR (KBr): $\tilde{\nu}$ = 1783, 1706, 1655, 1532, 1404, 1342 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.65 (s, 2H), 5.49−4.79 (m, 4H), 3.56−3.13 (m, 10H), 2.68−2.45 (m, 6H), 1.12−1.08 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.5, 199.9, 184.8, 184.7, 184.5, 173.7, 173.4, 172.8, 172.7, 171.3, 171.2, 170.8, 170.7, 170.5, 166.6, 164.5, 164.4, 151.3, 150.5, 150.2, 135.0, 133.9, 133.0, 132.7, 132.4, 132.3, 124.8, 60.3, 60.2, 59.5, 59.2, 52.0, 51.2, 48.6, 37.7, 35.6, 35.5, 13.2, 13.1, 13.0. MS (FAB^+): m/z (%) 1033 (M^+ + 1, 49), 923 (25), 586 (38), 445 (18). HRMS (LSIMS): m/z 1032.8699; calcd for $[C_{34}H_{28}N_6O_8S_{12} + H]^+$, 1032.8690. Anal. Calcd for $C_{34}H_{28}N_6O_8S_{12}$: C 39.52, H 2.73, N 8.13. Found: C 39.64, H 2.82, N 8.02.

(2*Z*/*E*)(2′*Z*/*E*)(3a*R*,3a′*R*,6a*S*,6a′*S*)-5,5′-(((2-((3a*R*,6a*S*)(*E*/*Z*)-2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)-4,6-dioxotetrahydro-5*H*-[1,3]dithiolo[4,5-*c*]-pyrrol-5-yl)ethyl)azanediyl)bis(ethane-2,1-diyl))bis(2-(4-ethyl-3-oxo-6-thioxo-3*H*,4*H*-[1,2]dithiolo[3,4-*b*][1,4]thiazin-5(6*H*)-ylidene)dihydro-4*H*-[1,3]dithiolo[4,5-*c*]pyrrole-4,6(5*H*)-dione) (16). 7 mg (10%) by method A or 28 mg (20%) by method B or 90 mg (43%) by method C, orange solid, mp 197−198 °C (dec.) (DCM/EtOAc 50:50), mixture of conformers. IR (KBr): $\tilde{\nu}$ = 1781, 1710, 1670, 1540, 1404, 1340 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 5.73−4.72 (m, 6H), 3.67−3.07 (m, 12H), 3.07−2.16 (m, 6H), 1.16−1.05 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.2, 185.1, 174.3, 164.4, 151.3, 133.4, 132.4, 60.7, 59.9, 52.3, 51.8, 51.6, 50.8, 49.0, 37.3, 13.3, 13.2. MS (FAB^+): m/z (%) 1356 (M^+ + 1, 24), 1005 (27), 923 (41), 682 (34), 433 (22). HRMS (LSIMS): m/z 1355.7396; calcd for $[C_{42}H_{33}N_7O_9S_{18} + H]^+$, 1355.7385. Anal. Calcd for $C_{42}H_{33}N_7O_9S_{18}$: C 37.18, H 2.45, N 7.23. Found: C 37.07, H 2.55, N 7.16.

Calculations. DFT calculations were performed with the hybrid method known as B3LYP, in which the Becke three-parameter exchange functional[24] and the Lee−Yang−Parr correlation functional[25] are used, as implemented in the Gaussian 03 (revision C.02) program suite.[26] Geometry optimizations and the nitrogen inversion barrier for the simplified model **3** and geometry optimizations for compounds **3a**, **3b**, and **3f** were calculated using the 6-31G(d) basis for all the atoms, whereas for the complex **3f**$[Hg]^{2+}$·MeCN the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LANL2DZ)[27] were used to describe Hg and the 6-31G(d) basis set was used for the rest of the atoms. Energy values for structures related to model **3** and compounds **3a** and **3b** were calculated by punctual calculations on the obtained geometries using the same functional and the 6-311+G(2d,p) basis set for all atoms. The transition state of the simplified model for **3** was confirmed by a vibrational analysis (one imaginary frequency) and an IRC calculation.[28]

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra of the products and coordinates of all stationary points for the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Dr. Stefano Marcaccini, who passed away on October 1, 2012.

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