

Studies on the Reactions of Thiocarbonyl *S*-Methanides with Hetaryl Thioketones

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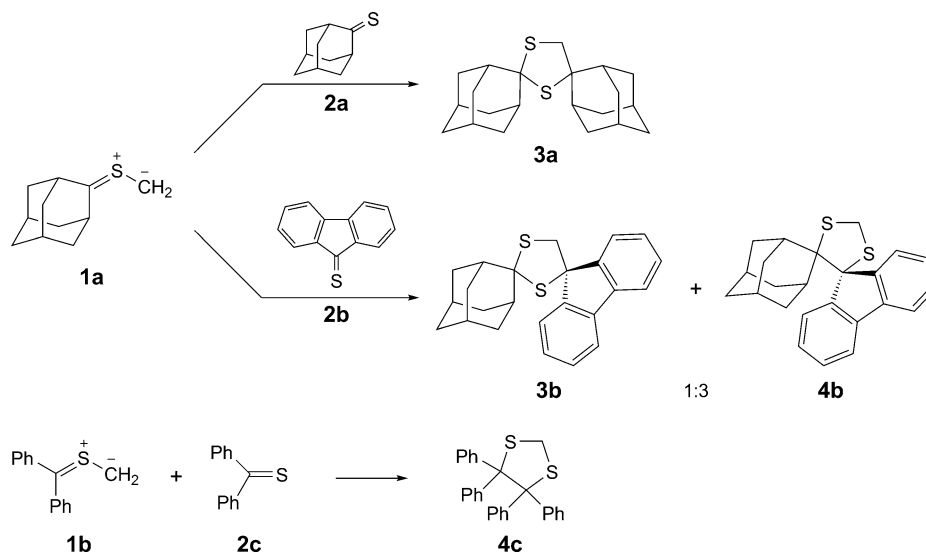
Dihetaryl thioketones react with thiocarbonyl ylides to give 1,3-dithiolanes in high yields. No competitive side reactions of the thiocarbonyl ylides were observed, evidencing the ‘superdipolarophilic’ character of this less-known group of thioketones. Depending on the type of substituents present in both the thiocarbonyl ylide and the thioketone, formal [3+2] cycloadditions occur with complete regioselectivity or with formation of a mixture of both regioisomers. Regioselective formation of the sterically more crowded 1,3-dithiolanes is explained *via* a mechanism involving stabilized 1,5-biradicals. In systems with less-efficient radical stabilization, *e.g.*, in the case of adamantanethione *S*-methanide, substantial violation of the regioselectivity was observed as a result of steric hindrance.

Introduction. – Thiocarbonyl ylides belong to the class of the so-called *S*-centered 1,3-dipoles, and they are widely used for the preparation of *S*-heterocycles with diverse sizes of the formed ring [1]. The reactive thiocarbonyl *S*-methanides, generated *via* thermal N₂ elimination from 2,5-dihydro-1,3,4-thiadiazoles, easily react with various dipolarophiles, and special attention is paid to their reactions with ‘superdipolarophilic’ thioketones [2]. These reactions, leading to 1,3-dithiolane derivatives (*Schönberg* reaction [3]), are of interest not only for the preparation of these products, but also for studies on organic reaction mechanisms. Important features of these reactions are the regioselectivity and the nature of the postulated intermediates. Whereas *S*-methanides of cycloaliphatic thioketones, *e.g.*, adamantane-2-thione *S*-methanide (**1a**), react with adamantane-2-thione (**2a**) to give the sterically less-hindered 2,2,4,4-tetrasubstituted 1,3-dithiolane of type **3a**, the reaction of **1a** with 9*H*-fluorene-9-thione (**2b**) gave a *ca.* 1:3 mixture of the regioisomeric 1,3-dithiolanes **3b** and **4b** in favor of the sterically more crowded isomer [4] (*Scheme 1*). On the other hand, *S*-methanides derived from aromatic thioketones, *e.g.*, thiobenzophenone *S*-methanide (**1b**), react with thiobenzophenone (**2c**) to give the 4,4,5,5-tetrasubstituted 1,3-dithiolane of type **4c** as the sole product [3a].

Recently, we described the synthesis and selected reactions of aryl/hetaryl and dihetaryl thioketones [5]. Unexpectedly, the experiments with CH₂N₂ revealed that the presence of a hetaryl substituent such as thiophen-2-yl, selenophen-2-yl, or furan-2-yl results in a spontaneous evolution of N₂ even at –60°. In contrast to thiobenzophe-

¹⁾ Part of the planned Ph.D. thesis of *P. P.*, University of Łódź.

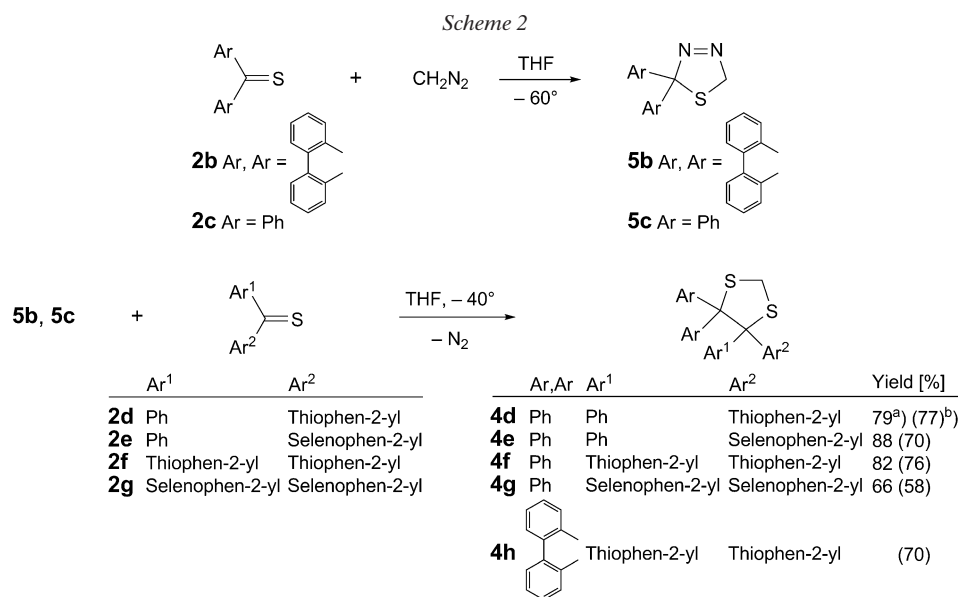
Scheme 1



none, the precursors of the corresponding *S*-methanides of type **1**, *i.e.*, 2,5-dihydro-2,2-diaryl-1,3,4-thiadiazoles **5** (*cf.* Scheme 2), could not be prepared in solution. Instead, a reactive intermediate trapped the starting thioketone **2** and yielded the sterically more crowded 1,3-dithiolane in a regioselective manner. However, in the case of phenyl selenophen-2-yl thioketone (**2e**), the formation of a second product, a novel macrocyclic dimer of the thiocarbonyl *S*-methanide was observed [6]. Based on these results, we proposed that the intermediate ‘thiocarbonyl ylide’ displays a biradical character. Thus, the formation of the twelve-membered cyclodimer can be considered as experimental evidence for the formation of a delocalized biradical. An earlier computational study suggested the participation of a 1,5-biradical in the formation of 1,3-dithiolane derivatives *via* formal [3+2] cycloaddition of thioketones with thiocarbonyl *S*-methanides [7].

The aim of the present study was the investigation of the formation of 1,3-dithiolanes *via* formal [3+2] cycloaddition of thiocarbonyl *S*-methanides and aryl/hetaryl and dihetaryl thioketones. Of special interest is the regioselectivity of the ring formation.

Results and Discussion. – The thermal decomposition of 2,2-disubstituted 2,5-dihydro-1,3,4-thiadiazoles **5** is considered as a straightforward method for the *in situ* generation of reactive thiocarbonyl *S*-methanides of type **1** [1a][8]. The stability of these precursors strongly depends on the type of substituents, and the presence of bulky cycloaliphatic groups allows them to be prepared as crystalline, shelf-stable compounds. On the other hand, 2,2-diaryl-substituted 2,5-dihydro-1,3,4-thiadiazoles **5** (Scheme 2) can be prepared only at low temperature and have to be used as thiocarbonyl *S*-methanide precursors at -40° without being isolated.



^a) Yield determined by ¹H-NMR with a weighed amount of 1,1,2,2-tetrachloroethane as a standard.

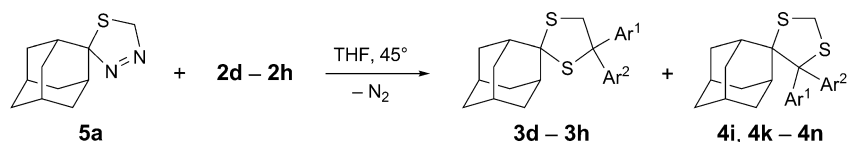
^b) Yield of isolated product.

According to the typical procedure for the generation of diaryl-substituted thiocarbonyl *S*-methanides of type **1b**, solutions of thiobenzophenone (**2c**) or 9*H*-fluorene-9-thione (**2b**) in THF were treated with CH₂N₂ at -60° . Equimolar amounts of hetarylphenyl, or dihetaryl thioketones, **2d** and **2e**, or **2f** and **2g**, respectively, were added to the colorless solutions, and the mixtures were warmed to -40° . After N₂ evolution had finished, the crude products were analyzed by ¹H-NMR spectroscopy with a weighed amount of 1,1,2,2-tetrachloroethane as a standard. In all reactions, only one product was obtained in good yields and identified as the sterically crowded 4,4,5,5-tetrasubstituted 1,3-dithiolane **4** (*Scheme 2*). The proposed structures of the products were elucidated from the characteristic absorption of the CH₂(2) group in the ¹³C-NMR spectra at 30.5–32.5 ppm [3].

In the second series, adamantane-2-thione *S*-methanide (**1a**) was generated from its precursor **5a** at 45° in THF in the presence of equimolar amounts of thioketones **2**. In all cases, the formation of mixtures of regioisomeric 1,3-dithiolanes was indicated by ¹H-NMR spectroscopy (weighed standard). In analogy to earlier reported products obtained from **1a** and aromatic thioketones **2c** and **2b** (*Scheme 1*), the major products were identified as the sterically more crowded 4,4,5,5-tetrasubstituted 1,3-dithiolanes of type **4** (*Scheme 3*). The isomer ratios **3/4** established by NMR spectroscopy were between *ca.* 1:3 and 1:4, and in the case of the mixtures of **3e/4k** and **3h/4n**, the major products **4k** and **4n**, respectively, were isolated as pure crystalline compounds and fully characterized.

Reactions with the 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methanide with hetaryl phenyl thioketones **2d** and **2e**, as well as with the dihetaryl thioketone **2h**, led

Scheme 3



Substrate	Ar ¹	Ar ²	Product and yield [%] ^{a)}		Yield of 3 + 4 [%] ^{b)}
2d	Ph	Thiophen-2-yl	3d (23)	4i (70)	82
2e	Ph	Selenophen-2-yl	3e (21)	4k (71)	80
2f	Thiophen-2-yl	Thiophen-2-yl	3f (16)	4l (75)	76
2g	Selenophen-2-yl	Selenophen-2-yl	3g (22)	4m (63)	64
2h	Thiophen-2-yl	Furan-2-yl	3h (21)	4n (70)	86

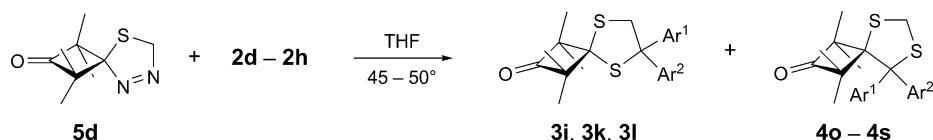
^{a)} Yield determined by ¹H-NMR with a weighed amount of 1,1,2,2-tetrachloroethane as a standard.

^{b)} Yield of isolated products (as a mixture of **3** and **4**).

also to mixtures of regioisomeric 1,3-dithiolanes **3** and **4**, with the sterically more crowded product of type **4** as the major component (*Scheme 4*). In comparison with the series of 1,3-dithiolanes obtained in the case of **1a** (*Scheme 3*), the ratio of isomers increased in favor of the sterically more crowded isomers of type **4**. However, the analogous reactions with di(thiophen-2-yl) thioketone (**2f**) and di(selenophen-2-yl) thioketone (**2g**) led to the sterically more crowded 1,3-dithiolanes **4r** and **4s**, respectively, as the sole products.

Finally, the structure of compound **4r**, deduced from the NMR data, was unambiguously confirmed by X-ray crystallography (*Fig.*). Although the molecule is achiral, the compound has crystallized in a chiral space group, and the absolute structure has been determined by the diffraction experiment. There are two symmetry-independent molecules in the asymmetric unit. Both molecules show disorder of the thiophene rings due to 180° rotation of each ring around its parent C–C bond. The five-membered dithiolane ring in each molecule has a half-chair conformation twisted on the C–C bond.

Scheme 4



Substrate	Ar ¹	Ar ²	Product and yield [%] ^{a)}		Yield of 3 + 4 [%] ^{b)}
2d	Ph	Thiophen-2-yl	3i (13)	4o (84)	94
2e	Ph	Selenophen-2-yl	3k (8)	4p (91)	95
2h	Thiophen-2-yl	Furan-2-yl	3l (6)	4q (91)	96
2f	Thiophen-2-yl	Thiophen-2-yl	–	4r (83)	81
2g	Selenophen-2-yl	Selenophen-2-yl	–	4s (95)	85

^{a)} Yields determined by ¹H-NMR with a weighed amount of 1,1,2,2-tetrachloroethane as a standard.

^{b)} Yield of isolated products (as a mixture of **3** and **4** or as pure compounds **4r** and **4s**).

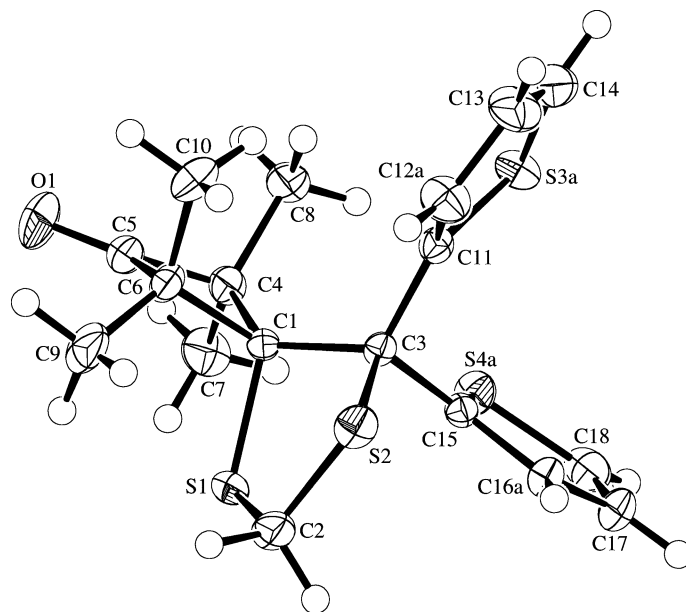
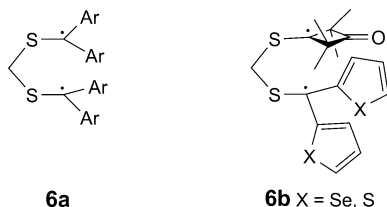


Figure. ORTEP Plot [9] of the molecular structure of one of the two symmetry-independent molecules of **4r** (with 50% probability ellipsoids; arbitrary numbering of the atoms; only the major conformations of the disordered thiophene rings are shown)

It is worth mentioning that the thiocarbonyl ylides **1a–1d** reacted with hetaryl thioketones **2** without competitive formation of 1,4-dithianes or thiiranes (see [1a][8]). These results confirm that hetaryl thioketones belong to the group of ‘superdipolarophiles’ in reactions with thiocarbonyl *S*-methanides [2]. According to *Huisgen*’s reactivity scale, the most reactive thioketone is 9*H*-fluorene-9-thione (**2b**), followed by thiobenzophenone (**2c**). For comparison purposes, the competition experiments of thiobenzophenone *S*-methanide (**1b**) with equimolar amounts of **2b** and di(thiophen-2-yl) thioketone (**2f**), as well as with **2c** and **2f**, were performed in THF at *ca.* -40° . The obtained products were analyzed by ^1H -NMR spectroscopy. In the first case, the only product formed was the sterically crowded 5,5-diphenylspiro[1,3-dithiolane-4,9’-[9*H*]fluorene [3b]. In the second experiment, however, the ratio of **4c/4f** was determined to be *ca.* 4:3. These results indicate that the symmetrical hetaryl thioketone **2f** is less reactive than 9*H*-fluorene-9-thione (**2b**), but almost as reactive as thiobenzophenone (**2c**).

Conclusions. – The present study revealed that hetaryl thioketones extend the group of ‘superdipolarophiles’ in reactions with thiocarbonyl *S*-methanides **1**. The observed regioselectivity of the 1,3-dithiolane formation evidences that the formal [3 + 2] cycloaddition occurs, most likely, *via* biradical intermediates. The latter mechanism leads to complete regioselectivity only when the heteroatom-containing substituents stabilize the biradical structure, *e.g.*, *via* delocalization in tetraaryl-substituted systems (*cf.* [6]). In such systems, the intermediate 1,5-biradical **6a** is the precursor of the

sterically crowded 4,4,5,5-tetrasubstituted 1,3-dithiolane, such as **4d–4h** [7] (cf. *Scheme 2*). The same regioisomers were only obtained as sole products in the reaction of 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methanide (**1c**) with dihetaryl thioketones **2f** and **2g**, which possess S- or Se-atoms in both heterocycles. In these cases, the stabilization of the 1,5-biradical intermediate **6b** results from delocalization within the hetaryl rings and, likely, from an additional stabilizing effect across the cyclobutanone ring [10]. The presence of Se- or S-atoms in the five-membered heteroaromatic rings is essential for the exclusive formation of an intermediate of type **6b** (see also [6]). Both heteroatoms are known to stabilize radicals in the α -position.



In the presented cases, electronic effects are decisive; however, in the reactions with adamantanethione *S*-methanide (**1a**), no radical stabilization is possible at the adamantane-substituted terminus of the intermediate. Accordingly, the influence of steric factors is of increasing importance, and the formation of the sterically less crowded 1,3-dithiolanes as minor products is also observed in all cases.

In summary, the results presented herein, additionally supported by computational studies [7], evidence that, in the case of S-centered thiocarbonyl ylides, some of the formal [3 + 2] cycloadditions occur stepwise *via* biradical intermediates. This conclusion supports the concept of the radical character of ‘1,3-dipolar cycloaddition reactions’ formulated by *Firestone* [11], at least for some systems with the required structural features.

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Experimental Part

1. *General*. M.p.: *MEL-TEMP. II* (Aldrich); uncorrected. Column chromatography (CC): silica gel (70–230 mesh; *Merck*). IR Spectra: *NEXUS* FT-IR instrument; in KBr; $\tilde{\nu}$ in cm^{-1} . ^1H - and ^{13}C -NMR spectra: *Bruker Avance III* instrument; at 600 and 150 MHz, resp., with the solvent signal as reference; in CDCl_3 ; δ in ppm; J in Hz; ad, adamantane. ESI-MS: *Varian 500 MS* LC ion trap spectrometer; in m/z (rel. %). Elemental analyses were performed in the Laboratory of the Faculty of Chemistry, University of Łódź; in%.

2. *Starting Materials*. 1,1,3,3-Tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one (**5d**) [12] and spiro[1,3,4-thiadiazole-2(5H),2'-tricyclo[3.3.1.1^{3,7}]decane] (**5a**) [13] were prepared by known methods. 9H-Fluorene-9-thione (**2b**), thiobenzophenone (**2c**), the nonsymmetrical heteroaromatic thioketones phenyl(thiophen-2-yl)methanethione (**2d**), phenyl(selenophen-2-yl)methanethione (**2e**), and (furan-2-yl)(thiophen-2-yl)methanethione (**2h**), as well as the symmetrical heteroaromatic thioketones di(thiophen-2-yl)methanethione (**2f**) and di(selenophen-2-yl)methanethione (**2g**) were obtained from the

corresponding ketones according to the known thionation procedure with *Lawesson's reagent* [5]. Other reagents used were commercially available.

3. *Reactions of Hetaryl Phenyl Thioketones 2d–2e or Dihetaryl Thioketones 2f–2g with 2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole (5c). General Procedure.* Thiobenzophenone (**2c**; 1 mmol) dissolved in 2 ml of THF was cooled to -70° and treated with small portions of ethereal CH_2N_2 soln. until the dark-blue color disappeared. A soln. of the corresponding thioketone **2d–2g** (1 mmol) in 2 ml of THF was added at -70° , and the mixture was kept in a cold bath (-45° to -40° , acetone/dry ice) for 2.5 h. Then, the mixture was allowed to warm slowly to r.t. During the reaction, a colorless precipitate was formed. The mixture was kept at r.t. for *ca.* 30 min. Then, the solvent was evaporated, and the crude product was purified by crystallization or by treatment with small portions of hexane.

3.1. *4,4,5-Triphenyl-5-(thiophen-2-yl)-1,3-dithiolane (4d).* Reaction with **2d**; purification by crystallization from CH_2Cl_2 /hexane. Yield: 320 mg (77%). Colorless crystals. M.p. $175.2\text{--}176.5^{\circ}$ (CH_2Cl_2 /hexane). IR: 3050w, 1597w, 1488m, 1440m, 1233m, 1033w, 747m, 722m, 708s. $^1\text{H-NMR}$: 3.01, 3.89 (*AB*, $J_{AB} = 9.6$, CH_2); 6.76–6.77 (*m*, 1 arom. H); 6.85 (*d*, $J = 3.6$, 1 arom. H); 7.10–7.20 (*m*, 10 arom. H); 7.39–7.43 (*m*, 4 arom. H); 7.50 (*d*, $J = 8.4$, 2 arom. H). $^{13}\text{C-NMR}$: 30.5 ($\text{CH}_2(2)$); 74.5, 78.3 ($\text{C}(4,5)$); 125.1, 125.6, 126.3, 126.4, 126.6, 126.7, 126.8, 127.0, 130.0, 130.6, 131.4, 131.8 (18 arom. CH); 142.3, 143.0 (*br.*, 4 arom. C). HR-ESI-MS: 416.072719 (M^+ , $\text{C}_{25}\text{H}_{20}\text{S}_2$; *calc.* 416.073100).

3.2. *4,4,5-Triphenyl-5-(selenophen-2-yl)-1,3-dithiolane (4e).* Reaction with **2e**; purification by crystallization from CH_2Cl_2 /hexane. Yield: 320 mg (70%). Colorless crystals. M.p. $177.4\text{--}178.8^{\circ}$ (CH_2Cl_2 /hexane). IR: 3049w, 1597w, 1489m, 1439m, 1232m, 1186w, 1083w, 1034w, 746m, 716s, 696s. $^1\text{H-NMR}$: 3.81, 3.90 (*AB*, $J_{AB} = 9.6$, CH_2); 7.00–7.01 (*m*, 2 arom. H); 7.07–7.19 (*m*, 9 arom. H); 7.37 (*d*, $J = 7.2$, 2 arom. H); 7.46–7.50 (*m*, 4 arom. H); 7.89 (*dd*, $J = 4.8$, 1.8, 1 arom. H). $^{13}\text{C-NMR}$: 30.6 ($\text{CH}_2(2)$); 76.4, 78.2 ($\text{C}(4,5)$); 126.2, 126.6, 126.7, 126.7, 126.9, 127.1, 127.9, 130.6, 131.6, 131.8, 131.9 (18 arom. CH); 142.7, 142.8 (*br.*, 4 arom. C). Anal. *calc.* for $\text{C}_{25}\text{H}_{20}\text{S}_2\text{Se}$ (463.53): C 64.78, H 4.35, S 13.83; found: C 64.55, H 4.38, S 13.75.

3.3. *4,4-Diphenyl-5,5-di(thiophen-2-yl)-1,3-dithiolane (4f).* Reaction with **2f**; purification by repeated treatment with small portions of hexane. Yield: 320 mg (76%). Colorless crystals. M.p. $192.7\text{--}193.4^{\circ}$. IR: 3095w, 3068w, 1595w, 1488m, 1440m, 1238m, 1086w, 849w, 747s, 734m, 707s. $^1\text{H-NMR}$: 3.94 (*s*, CH_2); 6.80 (*dd*, $J = 5.4$, 3.6, 2 arom. H); 7.03 (*dd*, $J = 3.6$, 1.2, 2 arom. H); 7.10–7.18 (*m*, 8 arom. H); 7.40–7.41 (*m*, 4 arom. H). $^{13}\text{C-NMR}$: 31.4 ($\text{CH}_2(2)$); 71.4, 79.1 ($\text{C}(4,5)$); 125.6, 125.7, 126.5, 126.9, 129.1, 131.4 (16 arom. CH); 142.2, 147.9 (4 arom. C). ESI-MS (MeOH): 461 (55, $[M + K]^+$), 445 (45, $[M + Na]^+$), 423 (100, $[M + H]^+$). Anal. *calc.* for $\text{C}_{23}\text{H}_{18}\text{S}_4$ (422.64): C 65.36, H 4.29, S 30.35; found: C 64.81, H 4.39, S 30.32.

3.4. *4,4-Diphenyl-5,5-di(selenophen-2-yl)-1,3-dithiolane (4g).* Reaction with **2g**; purification by repeated treatment with small portions of hexane. Yield: 310 mg (58%). Colorless crystals. M.p. $184.8\text{--}185.3^{\circ}$. IR: 3096w, 3050w, 1624w, 1487w, 1439m, 1227m, 1033w, 729m, 697s. $^1\text{H-NMR}$: 3.99 (*s*, CH_2); 7.08–7.09 (*m*, 2 arom. H); 7.13–7.19 (*m*, 6 arom. H); 7.30 (*dd*, $J = 4.2$, 1.2, 2 arom. H); 7.45–7.46 (*m*, 4 arom. H); 7.89 (*dd*, $J = 5.4$, 1.2, 2 arom. H). $^{13}\text{C-NMR}$: 31.6 ($\text{CH}_2(2)$); 75.2, 78.9 ($\text{C}(4,5)$); 126.5, 127.0, 128.3, 130.9, 131.5, 132.1 (16 arom. CH); 142.4, 145.0 (*br.*, 4 arom. C). Anal. *calc.* for $\text{C}_{23}\text{H}_{18}\text{S}_2\text{Se}_2$ (516.44): C 53.49, H 3.51, S 12.42; found: C 53.58, H 3.65, S 12.63.

4. *Reaction of Spiro[9H-fluorene-9,2'(5'H)-[1,3,4]thiadiazole] (5b) with di(thiophen-2-yl)methanethione (2f).* A soln. of **2b** (1 mmol) in 2 ml of THF was cooled to -70° and treated with small portions of a soln. of CH_2N_2 in Et_2O , until the green soln. became yellow. Then, a soln. of **2f** (1 mmol) in 2 ml of THF was added at -70° , and the mixture was kept in a cold bath (-45° to -40° , acetone/dry ice) for 1 h. Then, the mixture was allowed to warm slowly to r.t., whereby a colorless precipitate was formed. The mixture was kept at r.t. for *ca.* 30 min, then the solvent was evaporated, and the residue was crystallized from CH_2Cl_2 /hexane.

5,5-Di(thiophen-2-yl)spiro[1,3-dithiolane-4,9'-[9H]fluorene] (**4h**). Yield: 295 mg (70%). Colorless crystals. M.p. $216.4\text{--}218.0^{\circ}$ (CH_2Cl_2 /hexane). IR: 3066w, 2924w, 1624w, 1446m, 1427w, 1227m, 1239m, 1048w, 1034w, 851w, 789s, 745s, 736s, 719s, 706s. $^1\text{H-NMR}$: 4.50 (*s*, CH_2); 6.61 (*dd*, $J = 3.6$, 1.2, 2 arom. H); 6.74 (*dd*, $J = 5.4$, 3.6, 2 arom. H); 7.07–7.13 (*m*, 6 arom. H); 7.32–7.35 (*m*, 2 arom. H); 7.69 (*d*, $J = 7.2$, 2 arom. H). $^{13}\text{C-NMR}$: 32.5 ($\text{CH}_2(2)$); 70.3, 75.5 ($\text{C}(4,5)$); 119.8, 125.3, 125.7, 125.9, 127.5, 127.8, 128.6 (14 arom. CH); 140.2, 144.1, 147.9 (6 arom. C). ESI-MS (MeOH): 443 (100, $[M + Na]^+$).

5. Reactions of Hetaryl Phenyl Thioketones **2d–2e** or Dihetaryl Thioketones **2f–2h** with **5a**. *General Procedure*. Compound **5a** (1.1 mmol) and the corresponding thioketone **2** (1.05 mmol) were dissolved in freshly distilled THF (2.5 ml). The mixture was heated in an oil bath (45–50°), until the intense color of the thioketone vanished; the gas burette combined with the flask indicated the evolution of stoichiometric amounts of N₂. After removal of the solvent under vacuum, the residue was subjected to ¹H-NMR analysis in CDCl₃ soln. with a weighed amount of 1,1,2,2-tetrachloroethane as a standard. Crude products were purified by CC (CH₂Cl₂/petroleum ether (PE) 4:6). In all cases, formation of mixtures of regioisomeric 1,3-dithiolanes **3** and **4** was observed.

5.1. *Reaction with 2d: 5-Phenyl-5-(thiophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane] (4i; major) and 4-Phenyl-4-(thiophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane] (3d; minor) (crude product ratio 75:25). Reaction time: 8 h. Isolated as a mixture of isomers. Yield: 332 mg (82%). Yellow crystals. M.p. 139.8–141.0°. IR: 2905s, 2855s, 1443m, 1233w, 1220w, 1099w, 743w, 708w. ¹H-NMR: 1.19–3.04 (m, 28 H); 3.50, 3.56 (AB, J_{AB} = 9.0, CH₂ of **4i**); 3.83, 3.94 (AB, J_{AB} = 12.6, CH₂ of **3d**); 6.78–7.94 (m, 16 arom. H). ¹³C-NMR: 26.3, 26.4, 26.6, 26.8, 36.4, 36.8, 42.0, 42.1 (8 CH_(ad)); 27.2 (CH₂(2) of **4i**); 33.2, 33.6, 36.5, 36.6, 36.9, 37.6, 38.2, 38.9, 40.5 (10 CH_{2(ad)}); 50.2 (CH₂(5) of **3d**); 70.5, 75.4, 77.6, 78.5 (2 C(4), 2 C(5)); 124.8, 125.0, 126.0, 126.1, 126.6, 127.2, 127.4, 127.9, 128.1, 128.8, 130.8 (16 arom. CH); 140.8, 148.5 (2 arom. C of **4i**); 144.0, 151.2 (2 arom. C of **3d**). Anal. calc. for C₂₂H₂₄S₃ (384.63): C 68.70, H 6.29, S 25.01; found: C 68.37, H 6.00, S 25.01.*

5.2. *Reaction with 2e: 5-Phenyl-5-(selenophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane] (4k; major) and 4-Phenyl-4-(selenophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane] (3e; minor) (crude product ratio 77:23). Reaction time: 7 h. After chromatography, **4k** and **3e** were isolated as a mixture of regioisomers. Yield: 358 mg (80%). After repeated crystallization from hexane, **4k** was isolated in pure form. Colorless crystals. M.p. 152.1–153.0° (hexane). IR: 2903s, 2858m, 1441m, 1231m, 1221m, 709s, 695m, 684s. ¹H-NMR: 1.04–3.05 (m, 14 H); 3.54, 3.60 (AB, J_{AB} = 8.4, CH₂); 7.17–7.96 (m, 4 arom. H); 7.59 (d, ²J = 3.6, 1 arom. H); 7.83 (d, ²J = 6.6, 1 arom. H); 7.96 (br. s, 2 arom. H). ¹³C-NMR: 26.7, 26.9, 36.4, 37.1 (4 CH_(ad)); 27.5 (CH₂(2)); 33.2, 33.3, 38.0, 39.0, 40.8 (5 CH_{2(ad)}); 77.5, 77.6 (C(4,5)); 127.5, 128.0, 129.1, 130.5, 130.9, 131.0 (8 arom. CH); 140.8, 157.2 (2 arom. C). Anal. calc. for C₂₂H₂₄S₂Se (431.52): C 61.24, H 5.61, S 14.86; found: C 61.17, H 5.39, S 15.16.*

Spectroscopic Data of 3e (from the spectra of a mixture of 3e with the major product 4k). ¹H-NMR: 1.04–3.05 (m, 14 H); 3.78–3.96 (m, CH₂); 7.17–7.96 (m, 8 arom. H). ¹³C-NMR: 26.3, 26.4, 41.9, 42.0 (4 CH_(ad)); 36.3, 36.6, 36.6, 37.0, 37.6 (5 CH_{2(ad)}); 50.6 (CH₂(5)); 72.5, 78.5 (C(2,4)); 127.1, 127.4, 127.8, 127.9, 129.0, 130.7 (8 arom. CH); 144.2, 159.3 (2 arom. C).

5.3. *Reaction with 2f: 5,5-Di(thiophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane] (4l; major) and 4,4-Di(thiophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane] (3f; minor) (crude product ratio 82:18). Reaction time: 9 h. Isolated as a mixture of isomers. Yield: 309 mg (76%). Yellow crystals. M.p. 127.0–128.7°. IR: 2899s, 2851s, 1628w, 1442m, 1425m, 1225m, 1097m, 707s, 697s. ¹H-NMR: 1.48–2.82 (m, 28 H); 3.78 (s, CH₂ of **4l**); 3.93 (s, CH₂ of **3f**); 7.00–7.41 (m, 12 arom. H). ¹³C-NMR: 26.2, 26.3, 26.9, 35.6, 42.0 (8 CH_(ad)); 26.8 (CH₂(2) of **4l**); 32.9, 36.4, 36.7, 37.5, 38.8, 39.1 (10 CH_{2(ad)}); 52.4 (CH₂(5) of **3f**); 67.3, 72.0, 76.5, 79.0 (2 C(4), 2 C(5)); 125.1, 125.1, 125.9, 126.6, 127.7, 127.0 (12 arom. CH); 147.9 (2 arom. C of **4l**); 150.0 (2 arom. C of **3f**). ESI-MS (MeOH): 391 (100, [M + H]⁺).*

5.4. *Reaction with 2g: 5,5-Di(selenophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane] (4m; major) and 4,4-Di(selenophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane] (3g; minor) (crude product ratio 74:26.) Reaction time: 8 h. Isolated as a mixture of isomers. Yield: 325 mg (64%). M.p. 151.8–153.0°. IR: 2926s, 2899s, 2845s, 1625w, 1439m, 1234m, 1220m, 1097m, 717m, 695s, 703s. ¹H-NMR: 1.39–2.76 (m, 28 H); 3.72 (s, CH₂ of **4m**); 3.82 (s, CH₂ of **3g**); 7.07–7.81 (m, 12 arom. H). ¹³C-NMR: 26.3, 26.4, 27.0, 27.1, 35.7, 41.9 (8 CH_(ad)); 27.3 (CH₂(2) of **4m**); 33.1, 38.9, 39.1, 36.5, 36.7, 37.5 (10 CH_{2(ad)}); 53.4 (CH₂(5) of **3g**); 71.5, 79.3, 76.4, 76.4 (2 C(4), 2 C(5)); 127.7, 129.3, 131.0, 129.2, 130.1, 131.6 (12 arom. CH); 156.7 (2 arom. C of **3g**), 158.0 (2 arom. C of **4m**). Anal. calc. for C₂₀H₂₂S₂Se₂ (484.45): C 49.59, H 4.58, S 13.24; found: C 49.81, H 4.45, S 13.66.*

5.5. *Reaction with 2h: 5-(Furan-2-yl)-5-(thiophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane] (4n; major) and 4-(Furan-2-yl)-4-(thiophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane] (3h; minor) (crude product ratio 77:23). Reaction time: 5 h. After CC, **4n** and **3h** were isolated as a mixture of regioisomers. Yield: 340 mg (86%). After repeated crystallization from hexane, **4n** was*

isolated in pure form. Yellow crystals. M.p. 120.2–121.2°. IR: 2899s, 2853s, 1636w, 1449m, 1235m, 1149m, 1097m, 1021m, 751m, 727s, 693s. ¹H-NMR: 1.02–2.74 (m, 14 H); 3.73, 3.84 (AB, J_{AB} = 9.0, CH₂); 6.33 (dd, J = 3.0, 1.8, 1 arom. H); 6.75 (dd, J = 3.6, 1.2, 1 arom. H); 6.99 (dd, J = 5.4, 3.6, 1 arom. H); 7.20 (dd, J = 4.8, 1.2, 1 arom. H); 7.43–7.44 (m, 2 arom. H). ¹³C-NMR: 26.4 (CH₂(2)); 26.9, 27.2, 35.0, 35.7 (4 CH₂(ad)); 32.6, 33.1, 38.3, 39.2, 40.0 (5 CH₂(ad)); 69.8, 77.1 (C(4,5)); 111.0, 112.3, 124.8, 126.6, 127.5, 141.4 (6 arom. CH); 146.5, 152.1 (2 arom. C). Anal. calc. for C₂₀H₂₂OS₃ (374.59): C 64.13, H 5.92, S 25.68; found: C 64.05, H 6.00, S 25.65.

Spectroscopic Data of 3h (from the spectra of a mixture of **3h** with the major product **4n**). ¹H-NMR: 1.02–2.74 (m, 14 H); 3.75–4.03 (m, CH₂); 6.32–7.38 (m, 6 arom. H). ¹³C-NMR: 26.2, 26.4, 42.0, 42.1 (4 CH₂(ad)); 36.3, 36.5, 36.7, 36.9, 37.6 (5 CH₂(ad)); 48.8 (CH₂(5)); 65.5, 78.8 (C(2,4)); 109.0, 110.3, 125.1, 125.7, 126.6, 142.1 (6 arom. CH); 147.6, 155.8 (2 arom. C).

6. *Reactions of Hetaryl Phenyl Thioketones 2d–2e or Dihetaryl Thioketones 2f–2h with 5d. General Procedure.* A soln. of **5d** (1.1 mmol) and a thioketones **2d–2h** (1.05 mmol) in freshly dist. THF (2.5 ml) was heated in an oil bath (45–50°), until the color of the thioketone disappeared; a gas burette indicated the liberation of a stoichiometric amount of N₂. After removal of the solvent under vacuum, the residue was subjected to ¹H-NMR analysis in CDCl₃ with a weighed amount of 1,1,2,2-tetrachloroethane as a standard.

6.1. *Reaction with 2d: 1,1,3,3-Tetramethyl-8-phenyl-8-(thiophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one (4o; major) and 1,1,3,3-Tetramethyl-6-phenyl-6-(thiophen-2-yl)-5,8-dithiaspiro[3.4]octan-2-one (3i; minor)* (crude product ratio 86 : 14). Reaction time: 3.5 h. The crude mixture was purified by CC (CH₂Cl₂/hexane 4 : 6). Product isolated as a mixture of regioisomers. Yield: 372 mg (94%). Colorless crystals. M.p. 109.0–112.0°. IR: 1778s (C=O), 1636w, 1597w, 1443m, 1230m, 1164m, 1022m, 744m, 707s. ¹H-NMR: 1.26, 1.33, 1.36, 1.38, 1.47, 1.58, 1.65, 1.72 (8s, 8 Me); 3.62–3.66 (m, CH₂ of **4o**); 3.83, 3.92 (AB, J_{AB} = 12.0, CH₂ of **3i**); 6.86–7.82 (m, 16 arom. H). ¹³C-NMR: 22.3, 22.5, 24.6, 24.8, 24.8, 25.5, 25.68, 25.70 (8 Me); 26.8 (CH₂(6) of **4o**); 51.7 (CH₂(7) of **3i**); 66.5 (br.), 66.6, 67.0, 68.8 (br.) (2 C(1), 2 C(3)); 71.0, 74.5, 75.8, 76.1 (C(4), C(8) of **4o**, C(4), C(7) of **3i**); 125.2, 126.1, 126.3, 126.6, 127.4, 127.6, 127.7, 127.9, 128.1, 128.4, 129.1, 130.2 (16 arom. CH); 132.2, 134.1 (2 arom. C of **3i**); 143.4, 150.3 (2 arom. C of **4o**); 219.9 (C=O of **4o**); 220.1 (C=O of **3i**). Anal. calc. for C₂₀H₂₂OS₃ (374.59): C 64.13, H 5.92, S 25.68; found: C 64.02, H 5.93, S 25.95.

6.2. *Reaction with 2e: 1,1,3,3-Tetramethyl-8-phenyl-8-(selenophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one (4p; major) and 1,1,3,3-Tetramethyl-6-phenyl-6-(selenophen-2-yl)-5,8-dithiaspiro[3.4]octan-2-one (3k; minor)* (crude product ratio 92 : 8). Reaction time: 6.5 h. The crude product was crystallized from CH₂Cl₂/MeOH. Yield: 420 mg (95%). Colorless crystals. M.p. 140.0–142.0°. IR: 1170s (C=O), 1443m, 1227m, 1164w, 1020w, 706s, 695s. ¹H-NMR: 1.23, 1.25, 1.28, 1.31, 1.47, 1.61, 1.62, 1.71 (8s, 8 Me); 3.70–3.74 (m, CH₂ of **4p**); 3.78–3.92 (m, CH₂ of **3k**); 7.13–7.97 (m, 16 arom. H). ¹³C-NMR: 22.1, 22.5, 24.5, 24.8, 25.2, 25.5, 25.7, 25.8 (8 Me); 27.0 (CH₂(6) of **4p**); 52.1 (CH₂(7) of **3k**); 60.2, 65.4, 66.2, 69.7 (2 C(1), 2 C(3)); 67.1, 73.0, 76.1, 76.7 (C(4), C(8) of **4p**, C(4), C(7) of **3k**); 127.4, 127.5, 127.8, 128.0, 128.3, 128.4 (br.), 128.9, 129.1, 130.8 (br.), 130.9, 131.3, 131.7 (16 arom. CH); 140.8, 160.8, 143.5, 158.1 (4 arom. C); 219.7, 219.9 (2 C=O). Anal. calc. for C₂₀H₂₂OS₂Se (421.49): C 56.99, H 5.26, S 15.21; found: C 56.55, H 5.12, S 15.17.

6.3. *Reaction with 2h: 1,1,3,3-Tetramethyl-8-(furan-2-yl)-8-(thiophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one (4q; major) and 1,1,3,3-Tetramethyl-6-(furan-2-yl)-6-(thiophen-2-yl)-5,8-dithiaspiro[3.4]octan-2-one (3l; minor)* (crude product ratio 94 : 6). Reaction time: 4 h. The crude product was purified by CC (CH₂Cl₂/hexane 4 : 6). Yield: 370 mg (96%). Yellow crystals. M.p. 130.0–132.4°. IR: 1784s (C=O), 1464m, 1381s, 1227s, 1130m, 1074m, 1027s, 1016s, 808s, 742s, 695s, 593m. ¹H-NMR: 0.81, 1.24, 1.29, 1.34, 1.38, 1.45, 1.57, 1.59 (8s, 8 Me); 3.61–3.92 (m, CH₂ of **3l**); 3.86–3.90 (m, CH₂ of **4q**); 6.35–7.44 (m, 12 arom. H). ¹³C-NMR: 19.3, 22.1, 22.4, 23.3, 24.6, 24.7, 28.3, 28.9 (8 Me); 29.1 (CH₂(6) of **4q**); 50.6 (CH₂(7) of **3l**); 65.6, 66.6, 67.0, 67.3 (2 C(1), 2 C(3)); 65.0, 67.2, 76.8, 77.3 (C(4,8) of **4q**, C(4,7) of **3l**); 109.1, 110.4, 111.6, 112.0, 125.3, 125.7, 126.0, 126.2, 126.4, 126.8, 140.8, 142.4 (12 arom. CH); 146.8, 148.1, 155.0, 152.2 (4 arom. C); 219.4, 219.7 (2 C=O). Anal. calc. for C₁₈H₂₀O₂S₃ (364.55): C 59.31, H 5.53, S 26.39; found: C 58.93, H 5.19, S 26.04.

6.4. *Reaction with 2f: 1,1,3,3-Tetramethyl-8,8-di(thiophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one (4r).* The reaction was complete after 2 h. The solvent was evaporated, and the crude product was purified by

CC (CH₂Cl₂/hexane 4 : 6). Yield: 320 mg (81%). Colorless crystals. M.p. 140.6–141.5°. IR: 1774s (C=O), 1630w, 1385w, 1234m, 710s. ¹H-NMR: 1.45, 1.64 (2s, 4 Me); 3.80 (s, CH₂); 6.94–6.95 (m, 2 arom. H); 7.24–7.25 (m, 2 arom. H); 7.29–7.30 (m, 2 arom. H). ¹³C-NMR: 24.1, 26.5 (4 Me); 28.3 (CH₂(6)); 67.0 (C(1,3)); 70.1, 76.6 (C(4,8)); 125.7, 126.3, 127.8 (6 arom. CH); 148.2 (2 arom. C); 219.5 (C=O). Anal. calc. for C₁₈H₂₀OS₄ (380.62): C 56.80, H 5.30, S 33.70; found: C 57.02, H 5.52, S 33.68.

Suitable crystals for the X-ray crystal-structure determination were grown from MeOH in the refrigerator.

6.5. *Reaction with 2g*: 1,1,3,3-Tetramethyl-8,8-di(selenophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one (**4s**). The reaction was complete after 4 h. The crude product was crystallized from MeOH. Yield: 323 mg (85%). Pale yellow crystals. M.p. 157.0–158.0° (MeOH). IR: 1770s (C=O), 1442m, 1383m, 1232s, 1012m, 808m, 696s. ¹H-NMR: 1.45, 1.63 (2s, 4 Me); 3.86 (s, CH₂); 7.17–7.18 (m, 2 arom. H); 7.37–7.38 (m, 2 arom. H); 7.95–7.96 (m, 2 arom. H). ¹³C-NMR: 24.4, 26.8 (4 Me); 28.9 (CH₂(6)); 66.9 (C(1,3)); 74.2, 76.5 (C(4,8)); 129.0, 129.2, 132.4 (6 arom. CH); 156.6 (2 arom. C); 219.4 (C=O). Anal. calc. for C₁₈H₂₀OS₂Se₂ (474.41): C 45.57, H 4.25, S 13.52; found: C 45.84, H 4.32, S 13.55.

7. *Competition Experiments*. a) *Compound 2f* vs. *Compound 2b* with **5c**. A soln. of **2c** (1 mmol) in 2 ml of THF was cooled to –70° and treated with small portions of a soln. of CH₂N₂ in Et₂O, until the dark-blue color disappeared. Then, equimolar amounts of **2f** (1 mmol) and **2b** (1 mmol) dissolved in 3 ml of THF were added at –70°, and the mixture was kept at –45° to –40° (acetone/dry ice bath) for 2 h. Then, the soln. was allowed to warm slowly to r.t. and kept at r.t. for ca. 30 min, and then the solvent was evaporated. The residue was subjected to ¹H-NMR analysis in CDCl₃ with a weighed amount of 1,1,2,2-tetrachloroethane as a standard. The only observed product was the known 5,5-diphenylspiro[1,3-dithiolane-4,9'-[9H]fluorene] [**3b**]. Yield: 99% (¹H-NMR).

b) *Compound 2f* vs. *Compound 2c* with **5c**. In analogy to the procedure described above, a soln. of **2c** (0.57 mmol) in 2 ml of THF at –70° was treated with an ethereal CH₂N₂ soln., followed by a soln. of **2f** (0.57 mmol) and **2c** (0.57 mmol) in 3 ml of THF. The mixture was stirred at –45° to –40° for 2 h and then allowed to warm slowly to r.t. After 30 min at r.t., the solvent was evaporated, and the residue was subjected to ¹H-NMR analysis (CDCl₃; 1,1,2,2-tetrachloroethane as a standard). The crude product was identified as a mixture of the known 4,4,5,5-tetraphenyl-1,3-dithiolane (**4c**) [**3b**] (40%) and **4f** (29%; ¹H-NMR).

8. *X-Ray Crystal Structure Determination of 4r* (Table and Fig.)²⁾. All measurements were carried out on an Agilent Technologies SuperNova area-detector diffractometer [14] using MoK_α radiation (λ 0.71073 Å) from a micro-focus X-ray source and an Oxford Instruments Cryojet XL cooler. Data reduction was performed with CrysAlisPro [14]. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics [14] was applied. Equivalent reflections, other than Friedel pairs, were merged. The data collection and refinement parameters are compiled in the Table. A view of the molecule is shown in the Figure. The structure was solved by direct methods using SHELXS-2013 [15], which revealed the positions of all non-H-atoms. There are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher-symmetry space group using the program PLATON [16], but none could be found. Both molecules show disorder of both thiophene rings due to 180° rotation of each ring around its parent C–C bond, which swaps the positions of the S- and C-atoms in the 2,5-positions of the ring. Two positions were defined for these S- and C-atoms in each disordered ring, and the site occupation factors of the major orientations of these rings refined to 0.680(4) and 0.845(3) in molecule A and 0.954(3) and 0.794(3) in molecule B. Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered S- and C-atoms. In addition, the bond lengths involving disordered C-atoms were restrained to 1.40(1) Å. Neighboring disordered atoms between each orientation of the disordered thiophene rings were restrained to have similar atomic displacement parameters. One thiophene ring was additionally restrained to be planar. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and

²⁾ CCDC-1052007 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table. Crystallographic Data for Compound **4r**

Crystallized from	MeOH	$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	0.535
Empirical formula	C ₁₈ H ₂₀ OS ₄	Scan type	ω
Formula weight [g mol ⁻¹]	380.60	$2\theta_{(\text{max})}$ [°]	60.9
Crystal color, habit	colorless, prism	Transmission factors (min; max)	0.932; 1.000
Crystal dimensions [mm]	0.23 × 0.24 × 0.37	Total reflections measured	23111
Temp. [K]	160(1)	Symmetry-independent reflections	9322
Crystal system	monoclinic	Reflections with $I > 2\sigma(I)$	8753
Space group	$P2_1$	Reflections used in refinement	9322
Z	4	Parameters refined; restraints	499; 319
Reflections for cell determination	14706	Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0301
2θ Range for cell determination [°]	5–60	$wR(F^2)$ (all data)	0.0708
Unit cell parameters:		Weights	$w = [\sigma^2(F_o^2) + (0.0314P)^2 + 0.4989]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
a [Å]	8.69316(11)	Goodness-of-fit	1.039
b [Å]	12.82765(15)	Final $\Delta_{\text{max}}/\sigma$	0.001
c [Å]	15.94089(19)	$\Delta\rho$ (max; min) [e Å ⁻³]	0.55; –0.43
β [°]	90.7785(11)		
V [Å ³]	1777.45(4)		
D_x [g cm ⁻³]	1.422		

refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Refinement of the absolute structure parameter [17] yielded a value of 0.01(1), which confidently confirms that the refined model represents the true absolute structure. Neutral atom-scattering factors for non-H-atoms were taken from [18a], and the scattering factors for H-atoms were taken from [19]. Anomalous dispersion effects were included in F_c [20]; the values for f' and f'' were those of [18b]. The values of the mass attenuation coefficients are those of [18c]. The SHELXL-2014 program [21] was used for all calculations.

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