# PREPARATION AND REARRANGEMENT STUDY OF NOVEL THIOPHENIUM- AND SELENOPHENIUM-YLIDES

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*Dedicated to Dr. Alfred Bader on the occasion of his 85th birthday.*

A series of the title ylides was prepared by reaction of fused thiophene and selenophene derivatives with di-*tert*-butyl diazomalonate. Their thermal stability depended highly on their structure. While the terminal thiophenium- and selenophenium-ylides smoothly rearranged to the corresponding thiopyran and selenopyran derivatives, the internal thiophene ylides showed remarkable stability. The latter also exhibited hindered rotation around the S–C ylide bond and a high rotational barrier could be established in an NMR study.

**Keywords**: Heterocycles; Thiophene; Selenophene; Thiopyran; Selenopyran; Ylides; Rearrangement; Ring expansion.

A couple years ago[1–3] we studied [4π + 2π] cycloaddition reactions of fused vinylfurans and vinylthiophenes in order to synthesize higher-fused heterocycles utilizable in design of novel liquid crystals[4–6] and conductive organic materials[7–9]. When studying cycloaddition reactions of fused 2-vinylthiophenes with dimethyl acetylenedicarboxylate[2] we found that the cycloaddition afforded, besides the expected products of a [4+2] reaction, compounds possessing the fused cyclopenta[*b*]thiopyran (thialene) skeleton. A nonconcerted mechanism of such unprecedented thiophene-to-thiopyran ring expansion was suggested involving participation of thiophene sulfur atom and formation of a thiiranium ion in the course of the


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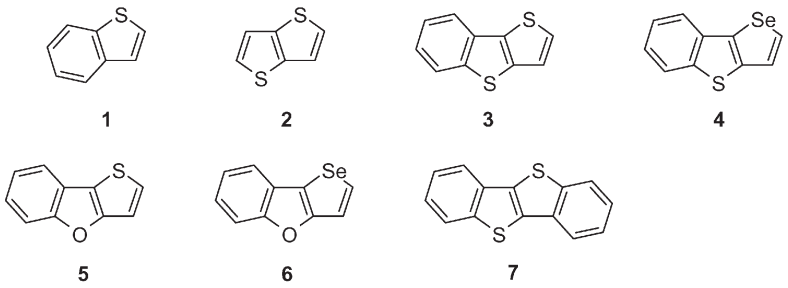
cycloaddition reaction. The abundance of the thiopyrans in the product mixture depended on the type of the aromatic ring fused to the thiophene ring and increased from benzene through thiophene, benzothiophene to benzofuran moiety. Formation of such a structurally related thiiranium species was also considered in various thiopyran-thiophene ring contractions[10–14] and in the Stevens rearrangement of thiophenium-ylides, the only known[15–18] thiophene-to-thiopyran ring expansion until now. It was also reported that the scope of the rearrangement was limited to simple thiophenium- and selenophenium-ylides[19], while benzothiophenium-ylides[16] did not rearrange to the corresponding benzothiopyran analogues. These results inspired us to perform a study of synthesis and reactivity of a series of novel thiophenium- or selenophenium-ylides, based on electron-rich fused thiophenes and selenophenes. We also dealt with some of the heterocycles earlier[2].

## RESULTS AND DISCUSSION

A series of model heterocycles was chosen – bicyclic benzo[*b*]thiophene (**1**) and thieno[3,2-*b*]thiophene (**2**), tricyclic thieno[3,2-*b*][1]benzothiophene (**3**), selenolo[3,2-*b*][1]benzothiophene (**4**), thieno[3,2-*b*][1]benzofuran (**5**) and selenolo[3,2-*b*][1]benzofuran (**6**), and finally tetracyclic [1]benzothieno-[3,2-*b*][1]benzothiophene (**7**).



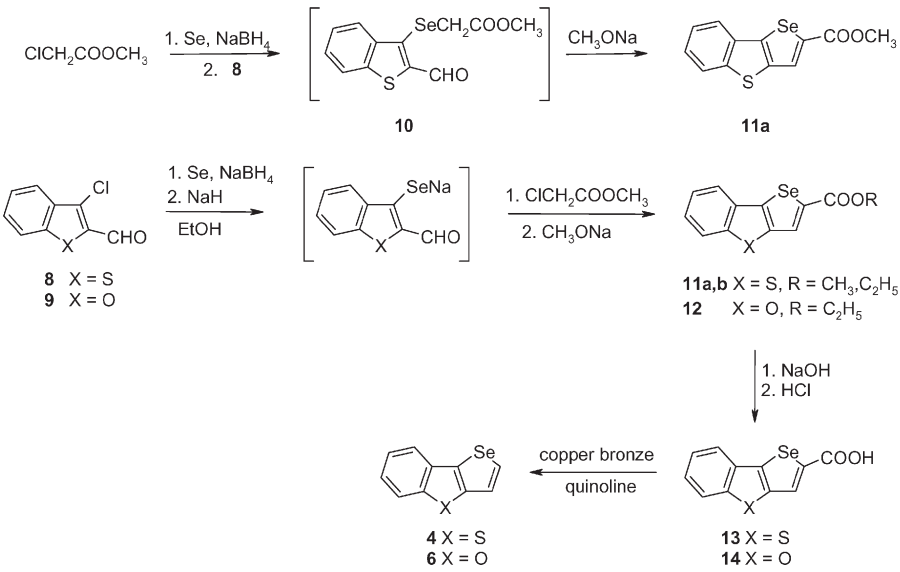

**1** **2** **3** **4**

**5** **6** **7**

While heterocycles **3** and **4** possess two competitive nucleophilic chalcogen atoms (S, Se) in the internal and terminal rings, in the fused derivatives **1**, **2**, **5**, **6**, the chalcogenophene ring is terminal. In heterocycle **7**, both of the thiophene rings are internal.

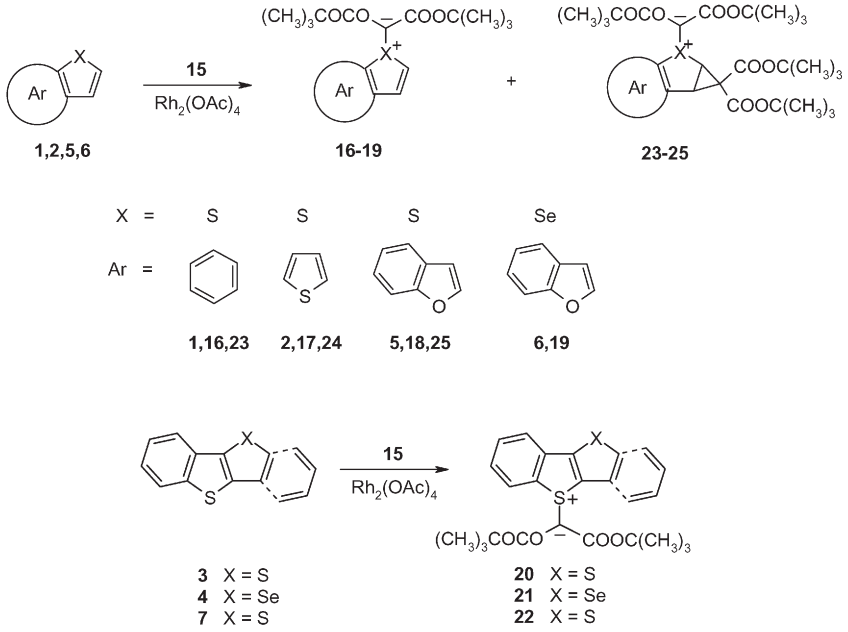
The starting heterocycles **2**–**7** were obtained by the published procedures[7,20–22]. Because of the inconvenient synthetic accesss[23,24] and lack of information[25] on the selenophene-derived heterocycles **4** and **6**, we elabo-

rated an improved one-pot synthesis, which excluded handling the hazardous intermediate selenides (Scheme 1). In the first method we used the freshly prepared sodium hydrogenselenide[26] which reacted with methyl chloroacetate and subsequently with 3-chlorobenzo[*b*]thiophene-2-carbaldehyde (**8**). The intermediate formyl ester **10** was immediately cyclized with sodium methoxide to ester **11a** in 32% yield. We found that a better one-pot method of the synthesis of heterocycle **4** was the nucleophilic aromatic substitution of chlorine atom in chloroaldehyde **8** with the in situ prepared sodium selenide and subsequent alkylation of the intermediate **12** with chloroacetate ester followed by a base-catalyzed cyclization. In the strongly basic medium, partial transesterification of the initially formed methyl ester **11a** was observed and finally a mixture of methyl **11a** and ethyl ester **11b** was obtained in the ratio ca. 2.5:1 in overall 90% yield. Due to fast decomposition of $NaBH_4$ in methanol it was not possible to replace ethanol by methanol as solvent in the effective preparation of the hydrogenselenide anion[27] to avoid the transterification reaction. The mixture of esters **11a**/**11b** was then hydrolyzed to acid **13**, the decarboxylation of which with copper bronze[23] in quinoline gave rise to heterocycle **4**. In the same way, the heterocycle **6** was obtained starting with 3-chlorobenzo[*b*]furan-2-carbaldehyde (**9**).



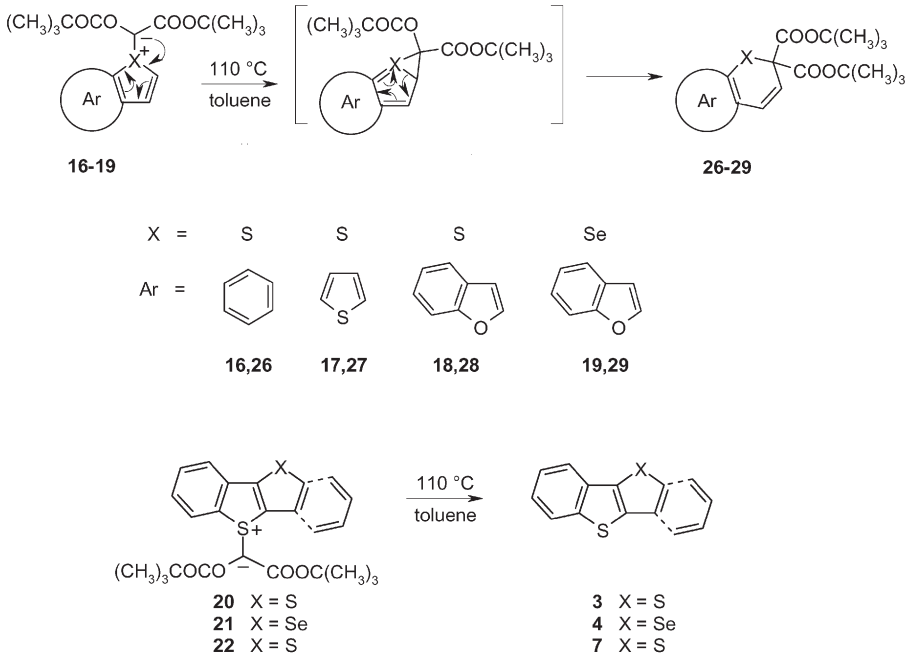

SCHEME 1

The ylides were formed by a rhodium acetate catalyzed reaction of heterocycles **1**–**7** with an excess of di-*tert*-butyl diazomalonate (**15**), a relatively stable[28] diazocarbonyl. With the exception of the benzofuran-fused chalcogenophenes **5** and **6**, heterocycles **1**–**4**, **7** smoothly afforded the corresponding stable ylides **16**, **17**, **20**–**22** (Scheme 2). Although the reaction was carried out at room temperature, ylides **18** and **19** could not be isolated, and obviously due to their low stability, only products of their successive rearrangement were obtained (vide infra). In no case, the formation of bis-ylides due to double alkylation of both the chalcogen atoms in **2**–**4**, **7** was observed. In addition, regardless of the type of chalcogen atom in **3** and **4**, alkylation proceeded regioselectively on the internal thiophene ring. In the reaction of **1**, **2**, and **5**, the major ylides were also accompanied by a small amount of products of their successive cyclopropanation **23**–**25**. Isolation of the cyclopropano derivative **25** indirectly proves formation of the corresponding but not isolable ylide **18**. Formation of a structurally related cyclopropano compound was already observed in the reaction of 2-*tert*-butylthiophene[29,30].




SCHEME 2

When studying the thermal rearrangements of ylides **16**–**22**, we have discovered significant differences in their reactivity. First we found that the thermal stability[16] of benzothiophenium-ylide **16** was limited to heating in a toluene solution, while in xylene a slow rearrangement proceeds to the corresponding benzothiopyran **26** along with dealkylation to benzothiophene (Scheme 3). Ylides **20**–**22** showed analogous stability; only slow dealkylation to the parent heterocycles **3**, **4**, and **7** was observed to the extent of ca. 25%. Such dealkylations leading to formation of the parent heterocycle and the corresponding carbene intermediate have already been described[31,32] and also utilized in cyclopropanation reactions.




SCHEME 3

In contrast to these stable ylides, the thienothiophene-derived ylide **17** rearranged smoothly on heating in toluene to thienothiopyran derivative **27** (55% yield). The highest reactivity was shown by benzofuran-fused ylides **18** and **19** which were formed by reaction of heterocycles **5** and **6** with diazomalonate **15** but immediately rearranged at room temperature to thiopyran **28** and selenopyran **29** derivatives.

The observed results are in good agreement with the postulated mechanism of the Stevens rearrangement of thiophenium-ylides[15]. Stability of ylides **16**, **20**–**22** can be explained by energetically disadvantgeous loss of benzene or thiophene (selenophene) aromaticity in the first step of the rearrangement, which evidently strongly disfavours the whole process. On the other hand, in ylides **17**–**19**, the presence of electron-rich fused thiophene and in particular furan rings stabilizes the formed thiiranium or seleniranium species and facilitates the thiophene and selenophene rearrangement. These results are in agreement with those obtained earlier where the electron-rich heterocycles fused to the thiophene ring strongly supported analogous thiophene-thiopyran rearrangement in the course of a cycloaddition reaction[2].

Structures of all products were unambiguously assigned by $^{1}H$ and $^{13}C$ NMR spectra and standard NMR experiments. In the ylides **16**–**22**, a characteristic shift of the ester carbonyl absorption in the IR spectrum to 1704–1707 $cm^{-1}$ was observed, which indicates the presence of an electron-rich centre bound to the α-position to the carbonyl group and thus formation of an S,C- or Se,C-ylide. The structure of ylide **21** was also proved by X-ray analysis of a single crystal (Fig. 1), which also revealed that the ylide is pyramidal and the angle between the plane of the ring and the ylide-carbon atom is 56°. This value is higher than that in simple thiophenium-ylides (50°)[15], but lower than in the corresponding sulfonium salts and sulfoxides. One of the *tert*-butyl ester group of the malonate grouping is located above the ring and the other is away from the ring. Such structural features leading to the

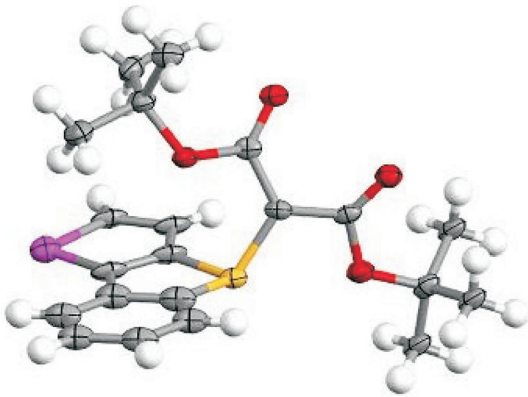


FIG. 1
View of the X-ray crystal structure of ylide **21**

stereoisomerism resulting from the restricted rotation about the ylidic S–C bond were also described in substitued thiophene and benzothiophene ylides[15,16].

In the $^{1}H$ and $^{13}C$ NMR spectra of **17**, only one sharp singlet of the *tert*-butyl groups and a single signal of carbonyl carbons appeared, which indicates that the rotation around the S–C bond is not substantially hindered, at least on the NMR timescale. On the other hand, spectral properties of ylides **20**–**22** were different. In their $^{1}H$ NMR spectra measured in deuteriochloroform on a 500 MHz instrument, they exhibited an extremely broad signal of the *tert*-butyl protons and two distinct signals of the carbonyl carbons appeared in their $^{13}C$ NMR spectra. When replacing deuteriochloroform with deuterated 1,1,2,2-tetrachloroethane, two broad singlets of *tert*-butyl groups appeared in all the ylides **20**–**22** at 25 °C which proved the nonequivalence of both ester groups. Coalescence of the signals of the *tert*-butyl groups in **20** was achieved at 313 K, while in **21** at 303 K and in **22** at 373 K, which corresponds to a rotational barrier of $\Delta G$ = 59, 57 and 70.5 kJ mol$^{-1}$, respectively.

It should be concluded that thiophenium-ylides can also be effectively prepared by a reaction of fused thiophene heterocycles with diazomalonate ester **15**. No competitive alkylation reaction was observed in heterocycles **3** and **4**; only alkylation on the internal thiophene ring proceeded. Unlike[33] only monoylides were formed with thienothiophenes and selenothiophene **2**–**4**. Ylides **20**–**22** exhibited high thermal stability and did not rearrange to thiopyran derivatives obviously due to a high energy barrier associated with the loss of aromaticity of the fused neighbouring benzene or thiophene (selenophene) in the initial step of the rearrangement process. Ylides **17**–**19** derived from the electron-rich heterocycles **2**, **5**, **6** smoothly rearrange to new fused thiopyrans **27**–**29**. Although it was postulated[15,34] that thiopyrans are the kinetic products of the rearrangement, neither of the prepared thiopyrans **26**–**29** rearranged on long-term heating in toluene to the corresponding 2-(thiophen-2-yl)malonates.

## EXPERIMENTAL

Melting points were determined on a Leica VM TG block and are uncorrected. Elemental analyses were carried out on a Perkin–Elmer 2400 instrument. IR spectra ($\nu$, cm$^{-1}$) were recorded on a Nicolet 740 FTIR spectrometer in chloroform. NMR spectra ($\delta$, ppm; *J*, Hz) were measured on a Varian Gemini 300 HC (300 MHz for $^{1}H$ and 75 MHz for $^{13}C$) and Bruker 500. Deuteriochloroform was used as solvent and the signals of the solvent served as internal standards. The 2D experiments, COSY, HMBC, HMQC, were carried out using pulse sequence and programme provided by the manufacturer.

X-ray data for **21**: $C_{21}H_{24}O_4SSe \cdot CHCl_3$, $M$ = 570.80 g mol$^{-1}$, monoclinic system, space group $P2_1/n$, $a$ = 11.428(2) Å, $b$ = 11.193(2) Å, $c$ = 19.649 (3) Å, β = 92.33 (1)°, $Z$ = 4, $V$ = 2511.2 (6) Å$^3$, $D_c$ = 1.510 g cm$^{-3}$, μ(CuKα) = 5.957 mm$^{-1}$, crystal dimensions of 0.06 × 0.22 × 0.37 mm. Data were collected at 150(2) K on a Xcalibur PX diffractometer with graphite monochromatized CuKα radiation. The structure was solved by direct methods[35] using the SHELX suite of programs[36], and anisotropically refined by full-matrix least-squares on $F^2$ values to final $R$ = 0.0877 and $R_w$ = 0.2502 using 5175 independent reflections ($\theta_{max}$ = 76.62°) and 320 parameters. The positions of disordered groups were found from the electron density maps. Disordered fragments were then placed in appropriate positions, and all distances between neighbouring atoms and angles were fixed. Because of lower quality of measured crystal, the disorder atoms of five-membered ring with Se were refined only isotropically and the residual density thanks to the presence of sulfur and selenium atoms is 1.27 e Å$^{-3}$. At the end of refinement, site occupancies were fixed and hydrogen atoms were placed in calculated positions.

CCDC 694269 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

*Caution! Many inorganic and organic selenium compounds are highly toxic. All operations should be conducted in an efficient hood. Gloves and appropriate protective clothes should be worn while performing these experiments.*

Methyl (**11a**) and Ethyl Selenolo[3,2-*b*][1]benzothiophene-2-carboxylate (**11b**)

*Method A.* To a slurry of grey selenium (1.6 g, 20.3 mmol) in ethanol (30 ml), $NaBH_4$ (1.54 g, 40.7 mmol) was added portionwise at 0 °C in argon atmosphere, and the mixture was stirred until $NaBH_4$ and the coloration diasappeared (no evolution of hydrogen appeared when a sample of the reaction mixture was acidified with 5% aqueous hydrochloric acid). Methyl chloroacetate (2.2 g, 20.3 mmol, 1.8 ml) was added and the mixture stirred at 0 °C for 2 h. Then a solution of sodium methoxide (0.55 g, 10.2 mmol) in methanol (40 ml) was added dropwise followed by addition of chloroaldehyde **8**[7] (1.0 g, 5.1 mmol) and heated to boiling for 2 h. The mixture was decomposed with water (50 ml) and extracted with ethyl acetate (3 × 30 ml). The combined organic solution was washed with water (30 ml), brine (2 × 30 ml), and dried with anhydrous magnesium sulfate. After evaporation, the crude product was purified by column chromatography (silica gel, toluene). 0.48 g (32%) of **11a** was obtained, m.p. 135–138 °C. For $C_{12}H_8O_2SSe$ (295.2) calculated: 48.82% C, 2.73% H; found: 49.05% C, 2.83% H. $^1$H NMR: 3.92 s, 3 H ($OCH_3$); 7.39 m, 1 H; 7.42 m, 1 H; 7.84 m, 2 H (H-5 and H-8); 8.24 s, 1 H (H-3). $^{13}$C NMR: 52.5 ($OCH_3$), 122.5 (CH), 123.7 (CH), 125.0 (CH), 125.9 (CH), 129.1 (CH), 134.7, 138.4, 138.6, 141.3, 143.0, 163.7 (C=O). IR: 3012, 2957, 2929, 2855, 1705 (C=O), 1518, 1444, 1436, 1339, 1319, 1278, 1257, 1240, 1149, 1096, 1067, 964, 928.

*Method B.* To a slurry of grey selenium (0.44 g, 5.6 mmol) in ethanol (30 ml), $NaBH_4$ (0.28 g, 7.3 mmol) was added portionwise at 0 °C in argon atmosphere, and the mixture was stirred until $NaBH_4$ and the coloration disappeared. Then sodium hydride (0.22 g, 55% in oil, 5 mmol) was added. After stirring for 5 min, a solution of chloroaldehyde **9**[7] (1.0 g, 5.1 mmol) in THF (5 ml) was added and the mixture was stirred at room temperature for 2 h. Then methyl chloroacetate (1.21 g, 11 mmol) was added, the mixture was further

stirred for 1 h, and finally sodium methoxide (0.55 g, 10.2 mmol) was added in one portion and the mixture was heated to boiling for 1 h. After cooling to room temperature, the mixture was decomposed with water (20 ml) and extracted with ethyl acetate (3 × 50 ml). The combined organic solution was washed with water (30 ml), brine (2 × 30 ml), and dried with anhydrous magnesium sulfate. After evaporation, the crude product was purified by column chromatography (silica gel, toluene). Yield 1.38 g (90%) of a mixture of methyl **11a** and ethyl ester **11b** in the ratio 2.5:1 was obtained. $^1$H NMR of **11b**: 1.40 t, 3 H, $J$ = 6.8 ($CH_3$); 4.37 q, 2 H ($OCH_2$); 7.34 m, 2 H (H-6 and H-7); 7.75 m, 1 H; 7.79 m, 1 H; 8.19 s, 1 H (H-3). $^{13}$C NMR: 14.2 ($CH_3$), 61.4 ($OCH_2$), 122.3 (CH), 123.6 (CH), 124.8 (CH), 125.6 (CH), 128.7 (CH), 134.6, 138.2, 139.2, 141.0, 142.9, 163.1 (C=O). IR: 2984, 2941, 2909, 1700 (C=O), 1518, 1469, 1444, 1413, 1369, 1338, 1319, 1274, 1256, 1240, 1149, 1064 m.

Selenolo[3,2-*b*][1]benzothiophene-2-carboxylic Acid (**13**)

A mixture of esters **11a**/**11b** (7.0 g), sodium hydroxide (9.1 g, 0.22 mol), water (60 ml) and methanol (40 ml) was heated to reflux under stirring for 2 h. After cooling to room temperature it was acidified with 10% aqueous hydrochloric acid (125 ml), the solid was filtered off and washed with water. Crystallization from ethanol afforded 5.73 g (90%) of acid **13**, m.p. 269–270 °C (m.p.[23] 268 °C). $^1$H NMR (DMSO-$d_6$): 7.40 m, 2 H; 7.79 s, 1 H (H-3); 7.91 dd, 1 H, $J_1$ = 7.3, $J_2$ = 1.7; 8.00 dd, 1 H, $J_1$ = 7.9, $J_2$ = 1.5.

Selenolo[3,2-*b*][1]benzothiophene (**4**)

A mixture of acid **13** (5.0 g, 17.8 mmol), copper bronze (0.5 g, 7.9 mmol) and freshly distilled quinoline (40 ml) was stirred at 160 °C for 1.5 h. When $CO_2$ evolution ceased, the mixture was cooled to room temperature and filtered, the filtrate was poured on a mixture of concentrated hydrochloric acid (40 ml) and ice and then extracted with hexane (3 × 100 ml). The combined hexane layers were washed with water (50 ml), brine (2 × 50 ml), and dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane) to afford 3.75 g (89%) of **4**, m.p. 114–115 °C (m.p.[23] 112 °C). $^1$H NMR (DMSO-$d_6$): 7.35 dt, 1 H, $J_1$ = 7.7, $J_2$ = 1.4; 7.41 dt, 1 H, $J_1$ = 7.6, $J_2$ = 1.4; 7.55 d, 1 H, $J$(2,3) = 5.5 (H-3); 7.80 dd, 1 H; 7.87 dd, 1 H; 8.10 d, 1 H (H-2). $^{13}$C NMR: 121.6 (CH), 122.8 (CH), 123.7 (CH), 124.3 (CH), 124.6 (CH), 131.6 (C-2), 135.1, 135.4, 139.1, 142.0. IR: 3106, 3065, 3009, 2925, 2853, 1601, 1469, 1441, 1335, 1253, 1209, 1171, 1064.

Ethyl Selenolo[3,2-*b*][1]benzofuran-2-carboxylate (**12**)

In the same way as for esters **11**, the reaction of grey selenium (1.86 g, 23.6 mmol), $NaBH_4$ (1.78 g, 47.2 mmol), sodium hydride (1.03 g, 55% in oil, 23.6 mmol), chloroaldehyde **9**[22] (3.87 g, 21.4 mmol), ethyl chloroacetate (5.77 g, 47.1 mmol), and sodium methoxide (2.58 g, 47.1 mmol) afforded after purification of the crude product by column chromatography (silica gel, toluene) 2.43 g (40%) of ethyl ester **12**, m.p. 95 °C (methanol) (m.p.[25] 91 °C). $^1$H NMR: 1.41 t, 3 H, $J$ = 7.0 ($CH_3$); 4.39 q, 2 H ($CH_2$); 7.33 dt, 1 H, $J_1$ = 7.7, $J_2$ = 1.2; 7.41 dt, 1 H, $J_1$ = 7.3, $J_2$ = 1.5; 7.59 ddd, 1 H, $J_1$ = 7.3, $J_2$ = 1.2, $J_3$ = 0.5; 7.72 ddd, 1 H; 8.15 s, 1 H (H-3). $^{13}$C NMR: 14.3 ($CH_3$), 61.6 ($OCH_2$), 112.5 (CH), 119.8 (CH), 120.4 (CH), 123.4 (CH), 125.5, 125.6, 126.2 (CH), 138.3, 158.2, 158.7, 163.4 (C=O). IR: 2984, 1698 (C=O), 1462, 1397, 1384, 1274, 1235, 1032.

Selenolo[3,2-*b*][1]benzofuran-2-carboxylic Acid (**14**)

Hydrolysis of **12** (2.4 g, 8.2 mmol) was achieved as for **13**. Crystallization from ethanol afforded 2.1 g (96%) of acid **14**, m.p. 273–274 °C (m.p.[25] 272 °C). $^1$H NMR (DMSO-$d_6$): 7.37 dt, 1 H, $J_1$ = 7.7, $J_2$ = 1.0; 7.45 dt, 1 H, $J_1$ = 7.3, $J_2$ = 1.4; 7.72 d, 1 H, $J$ = 7.3; 8.04 dd, 1 H, $J_1$ = 7.7, $J_2$ = 1.4; 8.25 s, 1 H (H-3); 13.35 bs, 1 H (OH).

Selenolo[3,2-*b*][1]benzofuran (**6**)

Decarboxylation of acid **12** (2.07 g, 7.8 mmol) by means of copper bronze (1.2 g, 18.7 mmol) and quinoline (20 ml) at 160 °C afforded after column chromatography (silica gel, hexane) 1.22 g (71%) of **6**, m.p. 60 °C (m.p.[25] 57 °C). $^1$H NMR: 7.34 m, 2 H; 7.49 d, 1 H, $J$(2,3) = 5.7; 7.60 m, 1 H; 7.69 m, 1 H; 7.98 d, 1 H, $J$(2,3) = 5.7. $^{13}$C NMR: 112.2 (CH), 114.6 (CH), 118.7, 119.4 (CH), 122.9 (CH), 124.3 (CH), 126.1, 131.2 (CH), 158.2, 160.2.

Preparation of Ylides. General Procedure

*A*. A mixture of benzo[*b*]thiophene (**1**) (0.49 g, 3.65 mmol), di-*tert*-butyl diazomalonate (**15**) (1.32 g, 5.47 mmol), rhodium acetate (5 mg) and 1,2-dichloroethane (5 ml) was stirred at room temperature for 16 h. After evaporation the residue was separated by column chromatography (silica gel, chloroform + 5% methanol) and afforded 1.06 g (83%) of **16** and 25 mg (1%) of **23**.

*Di-tert-butyl 2-(1λ$^4$-benzo[b]thiophen-1-ylidene)malonate* (**16**), m.p. 164–165 °C. For $C_{19}H_{24}O_4S$ (348.5) calculated: 65.49% C, 6.94% H; found: 65.23% C, 7.01% H. $^1$H NMR: 1.43 s, 18 H (6 × $CH_3$); 6.83 d, 1 H, $J$ = 5.8; 7.38 d, 1 H, $J$ = 5.8; 7.50 dt, 1 H, $J_1$ = 7.3, $J_2$ = 1.4; 7.56 dt, 1 H, $J_1$ = 7.3, $J_2$ = 1.3; 7.63 m, 1 H; 7.78 m, 1 H. $^{13}$C NMR: 28.2 (6 × $CH_3$), 51.5, 78.7 (2 quaternary C), 123.8 (CH), 125.4 (CH), 128.2 (CH), 128.9 (CH), 130.1 (CH), 133.3 (CH), 137.8, 137.9, 164.6 bs (2 × C=O). IR: 2980, 2931, 1705 (C=O), 1667, 1632, 1476, 1367, 1327, 1169, 1082, 1059, 1032.

*Di-tert-butyl 2-[1,1-bis(tert-butyloxycarbonyl)-1a,6b-dihydro-2λ$^4$-1H-benzo[b]cyclopropa[d]thiophen-2-ylidene]malonate* (**23**). For $C_{30}H_{42}O_8S$ (562.7) calculated: 64.03% C, 7.52% H; found: 64.12% C, 7.65% H. $^1$H NMR: 1.07 s, 9 H; 1.37 s, 18 H; 1.50 s, 9 H; 3.72 d, 1 H, $J$ = 6.7; 3.92 d, 1 H, $J$ = 6.7; 7.40 m, 1 H; 7.49 m, 2 H; 7.60 m, 1 H. $^{13}$C NMR: 27.3 (3 × $CH_3$), 27.9 (3 × $CH_3$), 28.7 (6 × $CH_3$), 39.9 (CH), 44.0, 49.2 (CH), 79.1 (2 quaternary C), 82.6, 84.0, 125.5 (CH), 127.3 (CH), 129.2 (CH), 130.9 (CH), 136.8, 138.21, 164.7 (C=O), 165.1 (C=O), 165.3 (2 × C=O) (1 quaternary C not detected). IR: 2978, 2931, 1724 (C=O), 1686, 1634, 1477, 1367, 1323, 1250, 1158, 1081, 1030.

*B*. Analogous reaction of ring system **2** (0.82 g, 5.9 mmol), diazomalonate **15** (1.7 g, 7 mmol) and rhodium acetate (5 mg) in 1,2-dichloroethane (5 ml) after chromatographic separation (silica gel, hexane, toluene, chloroform + 10% methanol) afforded 1.60 g (76%) of ylide **17** and 0.20 g (6%) of cyclopropano derivative **24**.

*Di-tert-butyl 2-(1λ$^4$-thieno[3,2-b]thiophen-1-ylidene)malonate* (**17**), m.p. 134–135 °C. For $C_{17}H_{24}O_4S_2$ (354.5) calculated: 57.60% C, 6.26% H; found: 57.52% C, 6.36% H. $^1$H NMR: 1.28 s, 18 H; 6.82 dd, 1 H, $J_1$ = 5.7, $J_2$ = 1.6; 7.23 dd, 1 H, $J_1$ = 5.2, $J_2$ = 0.6; 7.33 dd, 1 H, $J_1$ = 5.7, $J_2$ = 0.6; 7.54 dd, 1 H, $J_1$ = 5.2, $J_2$ = 1.6. $^{13}$C NMR: 27.9 (6 × $CH_3$), 50.4, 78.7 (2 quaternary C), 120.3 (CH), 127.9 (CH), 131.1 (CH), 132.2 (CH), 137.8, 142.7, 164.2 (2 × C=O). IR: 2 980, 2 930, 1706 (C=O), 1668, 1624, 1477, 1454, 1366, 1325, 1252, 1169, 1084, 1060.

*Di-tert-butyl 2-[1,1-bis(tert-butyloxycarbonyl)-2λ$^4$-1H-1a,5b-dihydrocyclopropa[b]thieno[d]thiophen-2-ylidene]malonate* (**24**), m.p. 166–167 °C. For $C_{28}H_{40}O_8S_2$ (568.8) calculated: 59.13% C, 7.09% H; found: 58.86% C, 7.19% H. $^1$H NMR: 1.10 s, 9 H; 1.31 s, 18 H; 1.40 s, 9 H; 3.72 d, 1 H, *J* = 6.7; 3.93 d, 1 H, *J* = 6.7; 6.81 d, 1 H, *J* = 5.3; 7.25 d, 1 H, *J* = 5.3. $^{13}$C NMR: 27.2 (3 × $CH_3$), 27.7 (3 × $CH_3$), 28.6 (6 × $CH_3$), 34.51 (CH), 44.8, 57.4 (CH), 62.9, 78.9 (2 quaternary C), 82.8, 84.1, 120.5 (CH), 131.8 (CH), 134.1, 143.7, 161.1 (C=O), 164.5 (C=O), 165.1 (2 × C=O). IR: 2982, 2932, 1722 (C=O), 1667, 1628, 1477, 1455, 1370, 1324, 1158, 1082, 1055, 1031.

*C.* Starting with ring system **3** (0.30 g, 1.6 mmol) and diazomalonate **15** (0.76 g, 3.2 mmol), after column chromatography (silica gel, chloroform + 10% methanol) 0.62 g (97%) of *di-tert-butyl 2-(4λ$^4$-thieno[3,2-b][1]benzothiophen-4-ylidene)malonate* (**20**) was obtained, m.p. 171–173 °C. For $C_{21}H_{24}O_4S_2$ (404.6) calculated: 62.35% C, 5.98% H; found: 62.15% C, 6.11% H. $^1$H NMR: 1.22 bs, 18 H; 7.30 d, 1 H, *J*(2,3) = 5.2; 7.45 m, 1 H; 7.53 d, 1 H, *J*(2,3) = 5.2; 7.58 m, 1 H; 7.67 d, 1 H, *J* = 7.6; 7.77 d, 1 H, *J* = 7.9. $^{13}$C NMR: 28.5 (6 × $CH_3$), 54.0, 78.6, 121.2 (CH), 121.6 (CH), 124.8 (CH), 127.5 (CH), 130.1 (CH), 130.6 (CH), 133.3, 136.3, 142.1, 142.5, 166.8 (C=O), 171.3 (C=O). IR: 2996, 2976, 2931, 1728 (C=O), 1705 (C=O), 1667, 1633, 1476, 1454, 1390, 1366, 1327, 1167, 1084, 1059.

*D.* In the same way, ring system **4** (0.50 g, 2.1 mmol) and diazomalonate **15** (1.02 g, 4.2 mmol) afforded after purification by column chromatography (silica gel, chloroform + 10% methanol) 0.92 g (97%) of *di-tert-butyl 2-(4λ$^4$-selenolo[3,2-b][1]benzothiophen-4-ylidene)malonate* (**21**), m.p. 184–187 °C. For $C_{21}H_{24}O_4SSe$ (451.5) calculated: 55.87% C, 5.36% H; found: 55.71% C, 5.44% H. $^1$H NMR: 1.19 bs, 18 H; 7.44 m, 1 H; 7.49 d, 1 H, *J*(2,3) = 5.6 (H-3); 7.59 m, 2 H; 7.76 d, 1 H, *J* = 7.8; 8.17 d, 1 H (H-2). $^{13}$C NMR: 28.3 (6 × $CH_3$), 54.3, 78.8, 122.6 (CH), 123.2 (CH), 124.8 (CH), 127.7 (CH), 130.8 (CH), 135.0 (CH), 135.8, 138.3, 141.3, 145.7, 165.0 (broad). IR: 2978, 2928, 1704 (C=O), 1666, 1633, 1476, 1366, 1327, 1083, 1059, 1032.

*E.* By the same procedure, ring system **7** (0.4 g, 1.66 mmol) and diazomalonate **15** (0.6 g, 2.50 mmol) afforded after column chromatography (silica gel, chloroform and then chloroform + 10% methanol) 0.74 g (97%) of *di-tert-butyl 2-(5λ$^4$-benzothieno[3,2-b][1]benzothiophen-4-ylidene)malonate* (**22**), m.p. 105–107 °C. For $C_{25}H_{26}O_4S_2$ (454.6) calculated: 66.05% C, 5.76% H; found: 66.07% C, 5.72% H. $^1$H NMR: 0.76 s, 9 H; 1.65 s, 9 H; 7.48 m, 2 H; 7.54 m, 1 H; 7.63 dt, 1 H, $J_1$ = 7.4, $J_2$ = 1.1; 7.73 m, 1 H; 7.84 m, 1 H; 7.93 m, 2 H. $^{13}$C NMR: 27.74 (3 × $CH_3$), 28.76 (3 × $CH_3$), 53.40, 78.12, 79.40, 121.57 (CH), 122.56 (CH), 123.86 (CH), 124.82 (CH), 125.98 (CH), 126.04 (CH), 128.28 (CH), 130.15, 130.77 (CH), 131.81, 133.73, 142.06 (2 quaternary C), 142.71, 162.43 (C=O), 166.45 (C=O). IR: 2980, 1707 (C=O), 1667, 1632, 1367, 1328, 1169, 1084, 1059.

Reaction of Ring System **5** with Diazomalonate **15**

A mixture of compound **5** (0.39 g, 2.24 mol), diazomalonate **15** (0.81 g, 3.4 mmol) and rhodium acetate (5 mg) in 1,2-dichloroethane (5 ml) was stirred at room temperature for 16 h. The crude product after evaporation was separated by column chromatography (silica gel, chloroform, chloroform + 10% methanol). An amount of 0.14 g of the starting compound **5** was recovered, followed by 0.48 g (55%) of **28** and 0.06 g (5%) of **25**.

*Di-tert-butyl 2H-thiopyrano[3,2-b][1]benzofuran-2,2-dicarboxylate* (**28**), m.p. 121–122 °C. For $C_{21}H_{24}O_5S$ (388.5) calculated: 64.93% C, 6.23% H; found: 64.74% C, 6.15% H. $^1$H NMR: 1.47 s, 18 H; 5.99 d, 1 H, *J*(3,4) = 10.5 (H-3); 6.68 d, 1 H, *J*(3,4) = 10.5 (H-4); 7.24 m, 2 H; 7.40 dd, 1 H, $J_1$ = 7.4, $J_2$ = 1.7; 7.46 dd, 1 H, $J_1$ = 7.3, $J_2$ = 1.7. $^{13}$C NMR: 27.5 (6 × $CH_3$),

60.4, 83.5, 106.5, 111.4 (CH), 119.2 (CH), 119.3 (CH), 119.4 (CH), 123.0 (CH), 125.2 (CH), 125.9, 147.6, 154.3, 165.7 (C=O). IR: 2979, 2934, 1736 (C=O), 1450, 1369, 1255, 1148, 1065.

*Di-tert-butyl 2-[1,1-bis(tert-butyloxycarbonyl)-2λ$^4$-1H-1a,7b-dihydrocyclopropa[4,5]thieno[3,2-b]-[1]-benzofuran-2-ylidene]malonate* (**25**). For $C_{32}H_{42}O_9S$ (602.8) calculated: 63.77% C, 7.02% H; found: 63.72% C, 7.25% H. $^1$H NMR: 1.06 s, 9 H; 1.41 s, 18 H; 1.49 s, 9 H; 3.73 d, 1 H, $J$ = 6.5; 4.10 d, 1 H, $J$ = 6.5; 7.27 dt, 1 H, $J_1$ = 7.6, $J_2$ = 1.2; 7.34 dt, 1 H, $J_1$ = 7.6, $J_2$ = 1.5; 7.44 dd, 1 H, $J_1$ = 7.6, $J_2$ = 1.2; 7.52 dd, 1 H, $J_1$ = 7.6, $J_2$ = 1.5. $^{13}$C NMR: 27.2 (3 × $CH_3$), 27.8 (3 × $CH_3$), 28.7 (6 × $CH_3$), 29.9 ($CH_2$), 45.4, 56.0 ($CH_2$), 61.5, 79.2, 83.2, 84.6, 112.6 (CH), 112.7, 119.5 (CH), 121.8, 124.5 (CH), 125.7 (CH), 160.3, 161.2, 161.4, 164.1, 165.2 (1 quaternary C not detected). IR: 2979, 2932, 1726 (C=O), 1693, 1628, 1477, 1368, 1307, 1250, 1158, 1090, 1030.

In the same way, the selenophene derivative **6** (1.0 g, 4.52 mmol) afforded 0.21 g (11%) of *di-tert-butyl 2H-selenopyrano[3,2-b][1]benzofuran-2,2-dicarboxylate* (**29**). For $C_{21}H_{24}O_5Se$ (435.4) calculated: 57.93% C, 5.56% H; found: 57.99% C, 5.58% H. $^1$H NMR: 1.44 s, 18 H; 5.80 d, 1 H, $J$(3,4) = 11.0; 6.56 d, 1 H, $J$(3,4) = 11.0; 7.17 m, 2 H; 7.32 m, 2 H. $^{13}$C NMR: 27.61 (6 × $CH_3$), 55.59 (C-2), 83.56, 111.52 (CH), 120.03 (CH), 123.02 (CH), 125.10 (CH), 127.47, 128.9 (CH), 128.99 (CH), 147.86, 154.33, 166.25 (1 quaternary C not detected). IR: 2982, 2933, 1724 (C=O), 1522, 1370, 1162, 1023.

Di-*tert*-butyl 2*H*-benzo[*b*]thiopyran-2,2-dicarboxylate (**26**)

A solution of ylide **16** (0.63 g, 1.80 mmol) in dry xylene (10 ml) was heated to boiling for 2.5 h, the solvent was evaporated and the residue purified by column chromatography (silica gel, hexane/ethyl acetate 6:1). An amount of 0.15 g (62%) of the parent heterocycle **1** was recovered followed by 13 mg (21%) of **26**, m.p. 173–175 °C. For $C_{19}H_{24}O_4S$ (348.5) calculated: 65.49% C, 6.94% H; found: 65.27% C, 7.11% H. $^1$H NMR: 1.43 s, 18 H; 6.09 d, 1 H, $J$(3,4) = 10.2; 6.63 d, 1 H, $J$(3,4) = 10.2; 7.08 m, 3 H; 7.22 m, 1 H. $^{13}$C NMR: 27.14 (6 × $CH_3$), 58.9, 83.1 (2 quaternary C), 120.9 (CH), 125.7 (CH), 126.0 (CH), 128.5 (2 × CH), 129.2, 129.6, 129.8 (CH), 166.1 (2 × C=O). IR: 2982, 2935, 1731 (C=O), 1474, 1371, 1279, 1255, 1162, 1145, 1075, 1018.

Di-*tert*-butyl 2*H*-Thieno[3,2-*b*]thiopyran-2,2-dicarboxylate (**27**)

A solution of **17** (1.14 g, 3.2 mmol) in dry toluene (20 ml) was heated to boiling for 50 min. The solvent was evaporated and the residue purified by column chromatography (silica gel, hexane/ethyl acetate 4:1). 0.05 g (11%) of heterocycle **2** and 0.73 g (64%) of **27** were isolated, m.p. 67–69 °C. For $C_{17}H_{22}O_4S_2$ (354.5) calculated: 57.60% C, 6.26% H; found: 57.47% C, 6.41% H. $^1$H NMR: 1.43 s, 18 H; 5.86 d, 1 H, $J$(3,4) = 10.3 (H-3); 6.62 dd, 1 H, $J_1$ = 10.3, $J$ = 0.6 (H-4); 6.84 dd, 1 H, $J_1$ = 5.2, $J_2$ = 0.6 (H-7); 7.18 d, 1 H, $J$ = 5.2 (H-6). $^{13}$C NMR: 27.4 (6 × $CH_3$), 59.9, 82.9 (2 quaternary C), 116.1 (CH), 122.6 (CH), 124.5 (CH), 124.6, 125.1 (CH), 128.4, 165.8 (2 × C=O). IR: 2982, 1731 (C=O), 1477, 1395, 1371, 1278, 1259, 1159, 1143, 1083.

Thermal Stability of Ylides **20**–**22**

Ylide **20** (202 mg, 1 mmol) in dry toluene (10 mmol) was heated to boiling for 20 h. The solvent was evaporated and the residue separated by column chromatography (silica gel, elu-

tion with chloroform and then with chloroform + 10% methanol). Conpound **3** (24 mg, 25%) and unreacted ylide **20** (133 mg, 66%) were isolated.

In the same way reaction of ylide **21** (187 mg, 0.41 mmol) afforded 22 mg (23%) of **4** and 112 mg (60%) of **21**. Analogously, reaction of ylide **22** (129 mg, 0.283 mmol) afforded 16 mg (23%) of **7** along with 91 mg (71%) of unreacted **22**.

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