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A new approach to the synthesis of 2-vinylthiophenes and selenophenes; competition between free radical and anionic cycloaromatization of bridged di- and tetrapropargylic sulfides and selenides

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Abstract—A series of unknown di- and tetrapropargylic sulfides and selenides have been prepared. In the presence of *t*-BuOK in dry THF these compounds underwent isomerization to the corresponding diallenes, followed by a tandem anionic cyclization and aromatization to 2-vinylthiophene or selenophene derivatives. Some mechanistic studies indicated competition between free radical and anionic cycloaromatization. The latter is influenced by the nature of the bridging heteroatom, substitution of the allenyl group and base concentration.

1. Introduction

Rearrangements involving the cyclization of π and heteroatom bridged diallenes have received considerable attention over the last three decades.[1–3] An important mechanistic question related to these reactions has been whether the process is concerted or free radical in nature. The latter was suggested to apply for the cyclization of diallenic sulfones and sulfides.[4–11] In the past decade, considerable attention has been focused on cyclization reactions of diallenes or diacetylenes involving free radical species.[12–15] The trigger for renewed interest in this type of reaction was the elegant mode of action of the naturally occurring enediynes,[16–18] whose biological activity involves a diradical cycloaromatization.[19] Prompted by these studies, our interest in such rearrangements was also revived, especially in studying the effect of tandem cyclization and aromatization of some novel dipropargylic systems such as **1a–c**, which besides their potential biological activity, would also be of considerable synthetic and mechanistic interest. During the course of our studies, we found that in the presence of amine bases at room temperature, π-conjugated bis-propargylic selenides, sulfides, sulfoxides and sulfones undergo facile and high yielding isomerization to the corresponding diallenes, followed by tandem cyclization and aromatization via a probable diradical intermediate (for the case of γ-phenyl substitution, see Scheme 1).[20] Surprisingly, we have also found that the rate of cyclization step was independent of the nature of the bridging functionality.

As a natural extension of this tandem reaction of various π-conjugated bis-propargylic compounds, we decided to test the possibility of a double tandem process of tetrapropargylic systems, in order to prepare some more complex polycyclic aromatic compounds. This investigation resulted in some surprising and unprecedented findings.

2. Results and discussion

The synthesis of the required tetrapropargylic compounds **10a–d** is presented in Scheme 2. Thus, palladium-catalyzed coupling of propargyl alcohol with *p*-dibromobenzene afforded diol **8**.[21] Mesylation of **8** with methanesulfonyl chloride and triethylamine afforded dimesylate **9** in 72% yield. The latter was treated with potassium hydroxide and the appropriate propargyl thioacetate,[22] to yield the corresponding sulfides **10a** and **10c** in 85 and 62% yields, respectively. Finally, oxidation of bis-sulfides **10a**,**c** using oxone, led to the formation of bis-sulfones **10b** and **10d** in 53 and 63% yields, respectively.

We first examined the double cycloaromatization of bis-sulfone **10b**, in order to test its conversion to the appropriate anthracene or phenanthrene derivatives. However, this compound was so reactive that even in the presence of weak bases such as 2,6-lutidine at low temperatures it

Keywords: sulfur and selenium heterocycles; allenes; acetylenes; anionic cyclizations; radical cyclization.

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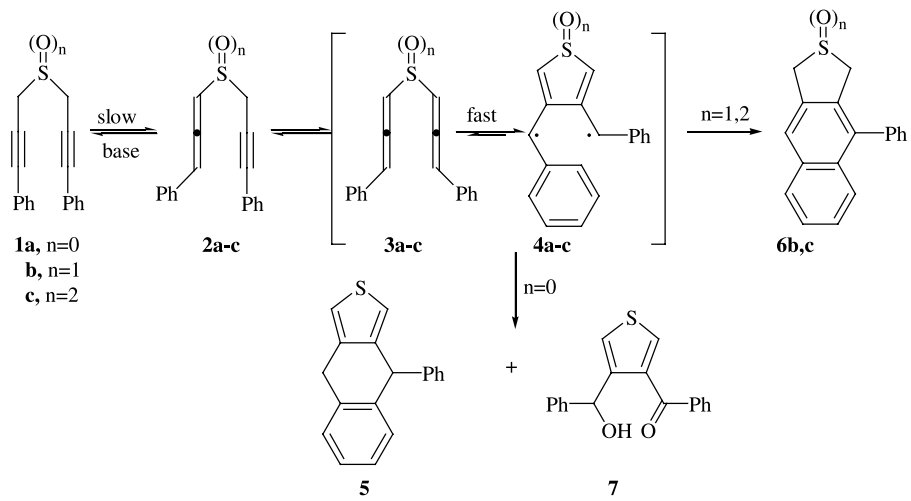
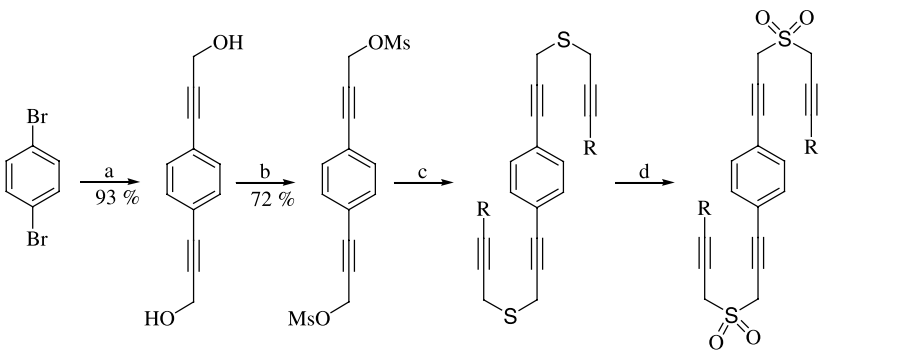


Scheme 1. Tandem isomerization, cyclization and aromatization of bridged propargylic compounds **1a**–**c**.

underwent decomposition. Therefore, we decided to test the reactivity of the corresponding bis-sulfide **10a**. The reaction of this compound under similar conditions used for bis-γ-phenylpropargyl sulfide (**1a**, DBU in acetonitrile), resulted in the formation of diketones **14a** and **15a** (1:1 ratio) but in only 8% yield each (Scheme 3). As already suggested in our previous report,[20b] for the formation of thienyl ketone **7**, formation of **14a** and **15a** may indicate similar behavior of the tetraradical intermediate which prefers to react with oxygen to yield the observed products via a hydroperoxide or cyclic peroxide precursor.

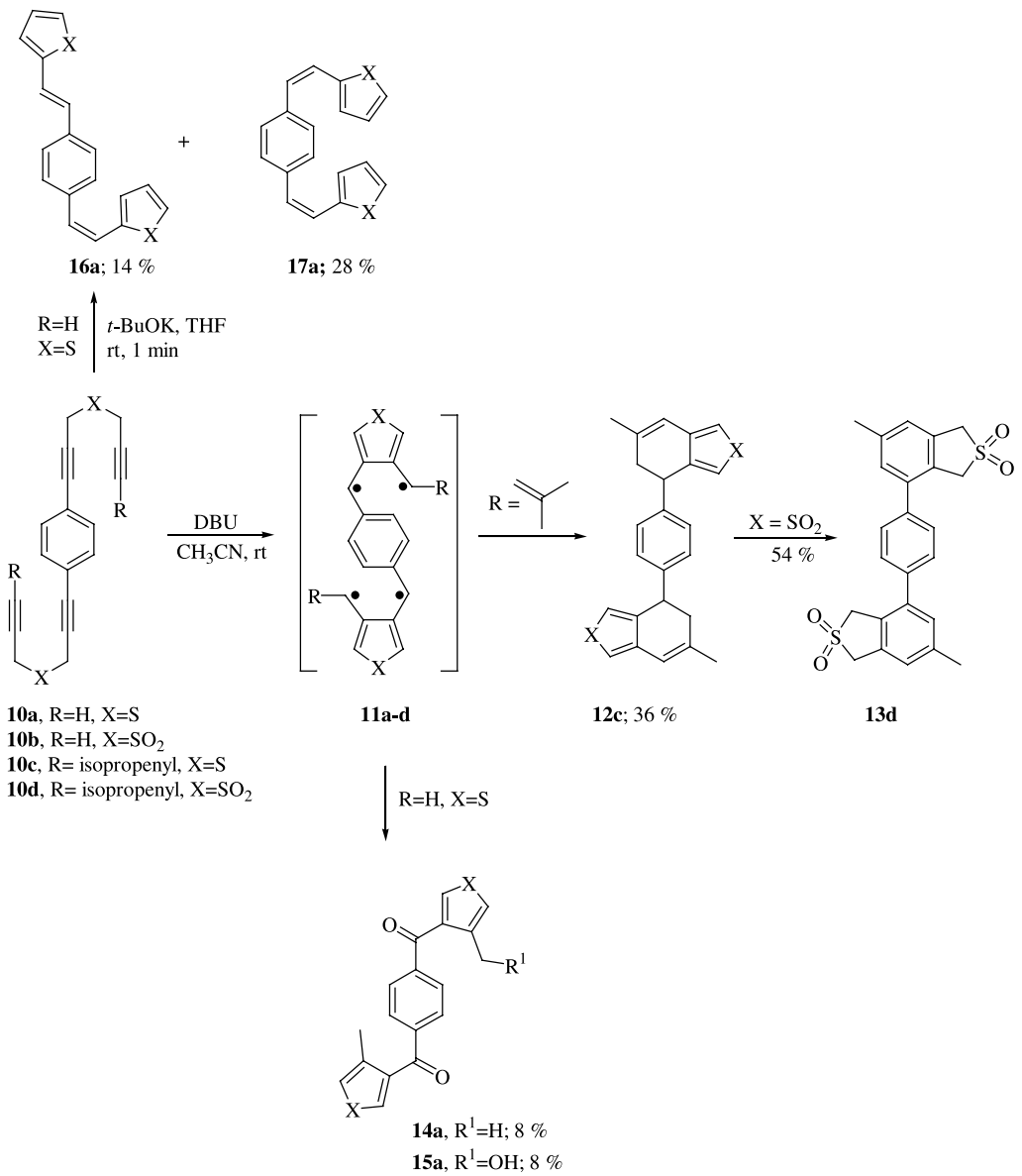
In sharp contrast to these results, treatment of bis-sulfide **10a** with *t*-BuOK in dry THF resulted in formation of the two conjugated cyclic aromatic products **16a** and **17a** in 14% and 28% yield, respectively. In spite of the extensive studies on the behavior of bridged dipropargylic systems under basic conditions,[11,23,24] there seems to be no precedent to this essentially spontaneous reaction at room temperature. Moreover, when the related tetrapropargylic sulfide **10c** was subjected to the action of *t*-BuOK in THF at room temperature, again, a fast reaction was observed as before, but no products analogous to **16a** and **17a** were observed. Interestingly, no intramolecular addition of the radical to the benzene ring takes place, but instead the tetraradical **11c** undergoes recombination to form **12c** (36% yield), a stable product. Similar behavior was observed for bis-sulfone **10d**, when treated with triethylamine in DMSO, which led to the formation of terphenyl compound **13d** in 54% yield. Recent studies from our group have shown that unsymmetrical dipropargylic sulfoxides underwent cyclization in both possible directions, presumably as a function of the relative reactivity of the appropriate diradical intermediates.[22] In general, when the latter involved a benzyl radical, the observed preference was recombination by intramolecular addition to an alkene rather than to a benzene ring; the preference is enhanced in a more polar solvent.

In view of the above mentioned results, we decided to study the scope of the new tandem reaction and its mechanism. Therefore, a number of substituted bridged dipropargylic sulfides and selenides was prepared, and their reaction with *t*-BuOK in THF investigated. The first such compound to be examined was the mono-γ-phenyl dipropargyl sulfide **18a**. This unsymmetrical dipropargylic sulfide reacted essentially instantaneously under these conditions and afforded a mixture of *cis*- and *trans*-2-styrylthiophenes **19a** and **20a** (1:1 ratio) in 70% yield (Scheme 4). The latter products have been synthesized before[25] and therefore, could be easily identified by their spectral data. Substitution of the acetylenic hydrogen in **18a** by a *t*-butyl group (**18b**) provided unambiguous structural proof of the thiophene



8 **9** **10 a,** R= H; 85 % **10 b**, R= H; 53 %
10 c, R= isopropenyl**;** 62 % **10 d**, R= isopropenyl**;** 63 %

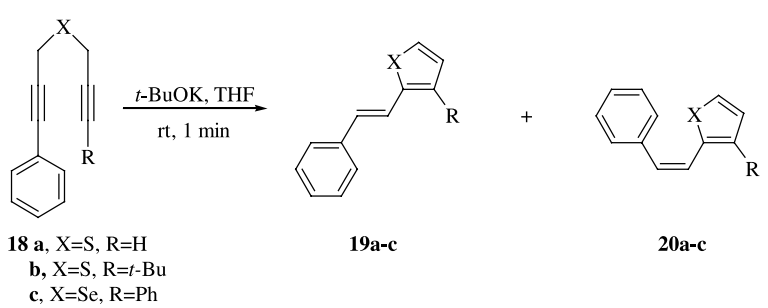
Scheme 2. Synthesis of tetrapropargylic systems. (a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, Et_3N, propargyl alcohol, 80°C, 4 h; (b) CH_3SO_2Cl, Et_3N, ether, 0°C, 1 h; (c) KOH, propargyl thioacetate, THF–MeOH, 25°C, 20 min; (d) oxone, H_2O–MeOH, 0–25°C, 1 week.



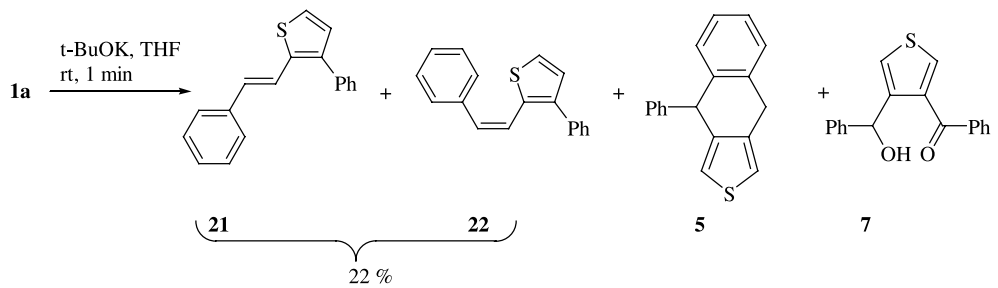
Scheme 3. Tandem reactions of tetrapropargylic systems **10a**–**d**.

products, and demonstrated the high regioselectivity of the reaction, namely bonding of the α-carbon of the phenyl substituted propargyl group to the γ-carbon of the unsubstituted or alkyl substituted propargyl group, but not vice versa (see also below for mechanism). Thus, reaction of sulfide **18b** with *t*-BuOK in dry THF at room temperature resulted in conversion to a mixture of the expected isomeric products **19b** and **20b** (2:3 ratio).

To further test the generality of this unusual reaction, we subjected bis-γ-phenyl-propargyl sulfide **1a** to the same reaction conditions. Compound **1a** was one of the first to be studied[20] using DBU as base in DMSO. On treatment with *t*-BuOK in dry THF, a mixture of products was obtained including the usual products of diradical cycloaromatization **5** and **7**, as well as products of the new cyclization, **21** and **22** (Scheme 5). The distribution of the products obtained in



Scheme 4. Reaction of dipropargylic compounds **18a**–**c** with *t*-BuOK in THF.



Scheme 5. Reaction of bis-γ-phenyl propargyl sulfide **1a** with *t*-BuOK in THF.

Table 1. Reaction of bridged dipropargylic systems with *t*-BuOK in THF

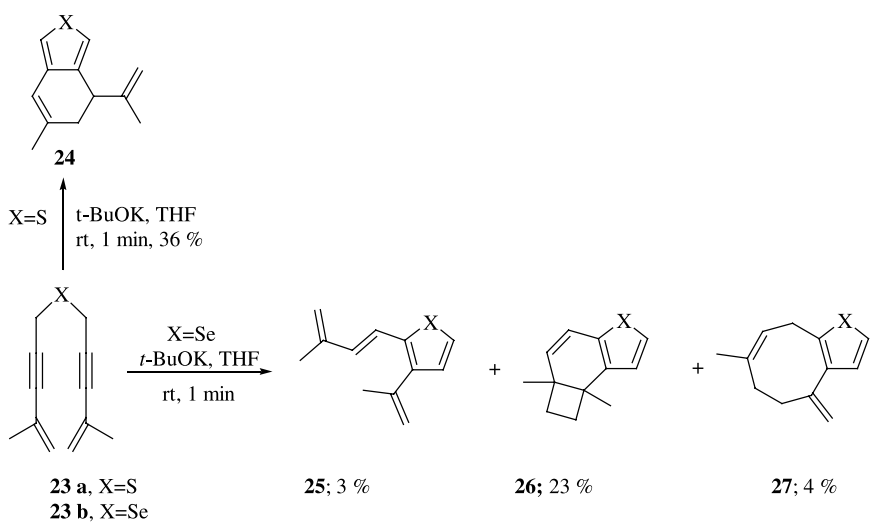
Entry	Substrate	*t*-BuOK (equiv.)	Product distribution (%)[a]	
			Anionic cyclization	Radical cyclization
1	**18a**	2	***E*-19a** (50)+***Z*-20a** (50)	–
2	**18b**	2	***E*-19b** (41)+***Z*-20b** (59)	–
3	**18c**	2	***E*-19c** (36)+***Z*-20c** (64)	–
4	**1a**	2.5	***E*-21** (27)+***Z*-22** (35)	{**5**+**7**} (38)
5	**1a**	1	***E*-21** (8)+***Z*-22** (9)	{**5**+**7**} (83)
6	**1a**	0.7	–	{**5**+**7**} (100)
7	**23a**	2	–	**24** (100)
8	**23b**	2	***E*-25** (10)+**26** (75.7)[b]+**27** (14.3)[b]	–

[a] The ratio of isomers was determined by ^{1}H NMR spectra and normalized to 100%.
[b] The *cis*-isomer is not stable under reaction conditions and underwent further rearrangements to **26** and **27**.

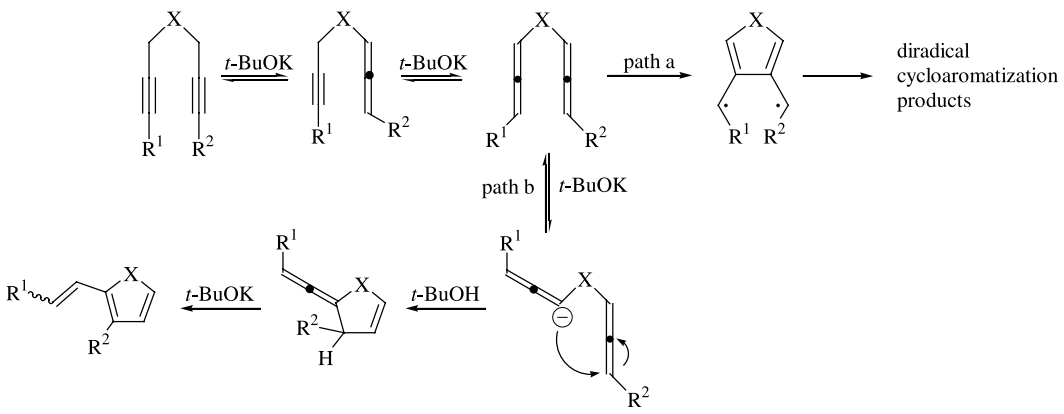
the last reaction exhibited high sensitivity to the base concentration as shown in Table 1. In sharp contrast to this behavior, the corresponding selenide **18c** yielded only the products expected from the 'new' cyclization, **19c** and **20c** (36:64 ratio), regardless of the base concentration.

Similarly to the reaction of **1a**, sulfide **23a** reacts readily with *t*-BuOK in THF. In this case, the only product obtained, was thiophene derivative **24**, which is the product of the free radical cycloaromatization (Scheme 6).[20] Here again, different behavior for the reaction of the related selenide **23b** was observed. Thus, in the reaction of **23b** with *t*-BuOK in THF, three products were obtained (**25**–**27**). While product **25** having a *trans*-configuration of double bonds is the one expected from the new anionic mechanism presented in Scheme 7, the other two products **26** and **27** seem to be derived from the *cis*-isomer of **25**. Presumably, this conjugated π-system is not stable under the reaction conditions and undergoes further cyclizations to the corresponding products **26** and **27**.

Inspection of the data presented in Table 1 indicates a general preference for the formation of the *cis*-isomer of 2-styrylthiophene products (entries 2–5, 8). Another significant observation is the effect of base concentration on the distribution of products obtained from bis-γ-phenylpropargyl sulfide (**1a**). For example, while using 0.7 equiv. of base (entry 6), only diradical cyclization is observed, raising the concentration of the base to 2.5 equiv. (entry 4), results in the formation of the 2-styrylthiophenes as the major products. Finally, dipropargylic systems bridged by selenium, such as **18c** (entry 3) and **23b** (entry



Scheme 6. Reaction of bis-propargylic compounds **23a**,**b** with *t*-BuOK in THF.



Scheme 7. Suggested mechanism for the formation of 2-vinylthiophenes and selenophenes from the reaction of di- and tetrapropargyl sulfides and selenides with *t*-BuOK in THF.

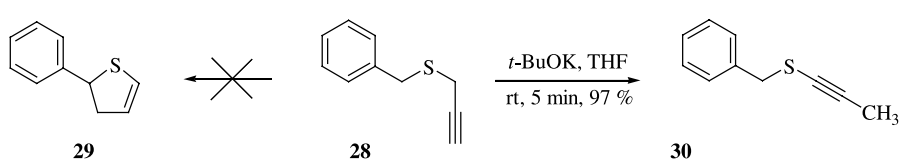
8), or those substituted by alkyl substituents (entry 2) exclusively undergo the new type of cyclization. We believe that the results described above, including the complete regiospecifity can be explained by the tentative mechanism presented in Scheme 7.

The reaction is initiated by a double base catalyzed propargyl–allene isomerization to yield the appropriate diallenyl sulfide or selenide. The latter can choose between two alternative routes. Path *a* leads to cycloaromatization via a diradical intermediate as previously described.[20] The other route (path *b*) involves deprotonation of the carbon atom α to the heteroatom. Next, the generated α-carbanion undergoes an intramolecular nucleophilic addition at the γ-allenic carbon of the other allenyl group with the formation of a 5-membered heterocyclic ring, which then by a series of base catalyzed prototropic shifts leads to the observed thiophene derivatives. The difference in behavior between the sulfide and the selenide may be a result of the lower aromatic resonance stabilization of selenophene vs thiophene,[26] that allows for the extension of the life span of the corresponding diallenic selenide and thus increases its chances for deprotonation. The competition of the anionic mechanism is thus influenced by the nature of the bridging moiety, substitution of the allenyl groups and the base concentration.

One may raise the question whether the involvement of the α-allenic carbanion is strictly necessary for the formation of the appropriate 5-membered heterocyclic ring, or whether the α-propargylic carbanion of the monoallenic sulfide can alternatively undergo a similar intramolecular nucleophilic addition to the γ-allenic carbon of the allenyl group. Therefore, a further mechanistic test to support the above mechanism has been advanced. We prepared benzyl propargyl sulfide **28** and subjected it to the action of *t*-BuOK in THF at room temperature. No cyclization product **29** was observed. Instead, sulfide **28** only isomerized to the acetylenic isomer **30** in 97% yield (Scheme 8). Interestingly, it was recently reported by Schwan and co-workers,[27] that compound **30** undergoes cyclization to **29**. However, this happened only in low yield under significantly more forcing conditions (heating with *t*-BuOK/acetonitrile solution for 24 h).

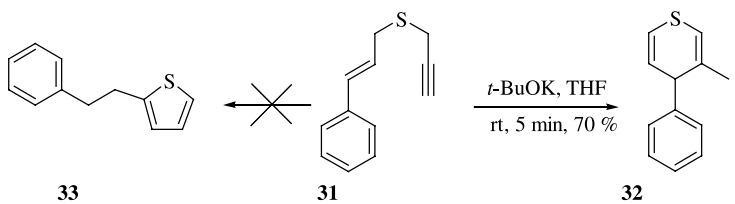
Furthermore, we have found that treatment of allyl propargyl sulfide **31** with *t*-BuOK in THF resulted in formation of the cyclic sulfide **32**, apparently, by nucleophilic addition of the appropriate allyl anion to the central carbon of the allenyl group (Scheme 9). Again, no cyclization product **33** was observed.

Finally, it is worthwhile to note that the novel anionic



29 **28** **30**

Scheme 8. Reaction of benzyl propargyl sulfide **28** with *t*-BuOK.



33 **31** **32**

Scheme 9. Reaction of allyl propargyl sulfide **31** with *t*-BuOK.

cyclization reported above has also been applied by us for the cyclization/aromatization of cyclic dipropargylic sulfides and selenides; the latter proceeds under similar reaction conditions and with good yields.[28]

In conclusion, we have discovered a new anionic cycloaromatization reaction of di- and tetrapropargyl sulfides and selenides, which is not only of considerable mechanistic interest but also of synthetic utility. It is also interesting to note that in spite of the detailed studies by Garratt,[11] Iwai[23] and Ollis[24] on bridged dipropargylic systems under practically identical condition, this type of anionic cycloaromatization had remained undiscovered.

3. Experimental

3.1. General

Melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 60 SXB FTIR. ^{1}H NMR and ^{13}C NMR were recorded on Bruker AC-200, DPX-300 or DMX-600 spectrometers in either $CDCl_3$ or other deuterated solvents, using TMS as internal standard. Chemical shifts are reported in δ units, and coupling constants in Hz. High-resolution mass spectra were obtained on a VG-Fison Autospec instrument. Other mass spectra were obtained on a Finningan GC/Ms 4021, with either electronic (EI) or chemical ionization (CI). Column chromatography was performed with Merck silica gel 60 (230–400 mesh), and TLC was run on precoated Merck silica gel plates 60 F254 (2.00 mm). Tetrahydrofuran was distilled from Na, diethyl ether was dried over Na wire. Other commercially available chemicals were used without further purification.

3.1.1. 3-(4-{3-[(Methylsulfonyl)oxy]prop-1-ynyl}-phenyl)-prop-2ynyl methanesulfonate (9). Diol **8**[21] (0.56 g, 3.0 mmol) and triethylamine (0.7 g, 6.9 mmol) were dissolved in dry diethyl ether (50 mL). After the mixture was cooled to 0°C, a solution of methanesulfonyl chloride (0.77 g, 6.8 mmol) in dry diethyl ether (10 mL) was added, and the reaction mixture was stirred for 3 h before it was warmed to room temperature and stirred for further 2 h. The reaction mixture was then diluted with chloroform, and washed with water (3×100 mL), 3% HCl (100 mL), 3% $NaHCO_3$ (100 mL) and water (3×100 mL). After drying over anhydrous $MgSO_4$, filtration and evaporation of the solvent, the desired dimesylate **9** was obtained as a yellow solid (0.74 g, 72% yield), which was recrystallized from ether as white crystals. Mp 128–129°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (s, 4H), 5.09 (s, 4H), 3.15 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.9 (CH), 122.2 (C), 88.3 (C), 83.0 (C), 57.9 (CH_2), 38.9 (CH_3); IR (KBr): 3023, 2222, 1500, 1361, 1174, 938 cm^{-1}; MS (EI): *m/z* 342 (M^+, 8%), 247 (100%), 151 (23%); HRMS calcd for $C_{14}H_{14}O_6S_2$ 342.0232; found 342.0245.

3.1.2. 1,4-Bis[3-(but-2-ynylthio)prop-1-ynyl]benzene (10a). A solution of KOH (0.52 g, 13 mmol) in methanol (20 mL) was slowly added to a magnetically stirred solution of propargyl thioacetate (0.75 g, 6.6 mmol)[22] and disulfonate **9** (1.12 g, 3.3 mmol) in THF (20 mL). After 40 min the reaction mixture was diluted with ether (100 mL), washed with water (3×100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give 0.82 g (85%) of bis-sulfide **10a** as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (s, 4H), 3.58 (s, 4H), 3.39 (d, *J*=2 Hz, 4H), 2.21 (t, *J*=2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.5 (CH), 122.7 (C), 86.2 (C), 82.9 (C), 79.1 (C), 71.5 (CH), 19.9 (CH_2), 19.0 (CH_2); IR (neat): 3010, 2212, 1478, 1184, 744 cm^{-1}; MS (CI): *m/z* 295 (MH^+, 31.7%), 223 (100%); HRMS calcd for $C_{18}H_{15}S_2$ 295.0612; found 295.0625.

3.1.3. 1,4-Bis{3-[(4-methylpent-4-en-2-ynyl)thio]prop-1-ynyl}benzene (10c). The title compound was prepared from **9** and γ-isopropenylpropargyl thioacetate[22] by the procedure described above, and obtained in 62% yield as yellowish viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (s, 4H), 5.29–5.30 (m, 2H), 5.23 (quintet. *J*=1.5 Hz, 2H), 3.66 (s, 4H), 3.60 (s, 4H), 1.89 (dd, *J*=1.5, 1 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.6 (CH), 126.4 (C), 122.7 (C), 122.1 (CH_2), 86.5 (C), 84.7 (C), 83.4 (C), 82.8 (C), 23.5 (CH_3), 20.2 (CH_2), 20.1 (CH_2); IR (neat): 2187, 1654 cm^{-1}; MS (CI): *m/z* 375 (MH^+, 42.5%), 263 (49.3%), 143 (100%); HRMS calcd for $C_{24}H_{23}S_2$ 375.1241; found 375.1210.

3.1.4. [3-(Prop-2-ynylthio)prop-1-ynyl]benzene (18a). The title compound was prepared from γ-phenylpropargyl bromide and propargyl thioacetate by the procedure described above, and obtained in 66% yield as colorless oil, after separation by column chromatography (silica gel, ethyl acetate–hexane 5:95). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.44 (m, 2H), 7.29–7.32 (m, 3H), 3.66 (s, 2H), 3.47 (d, *J*=2.4 Hz, 2H), 2.28 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.7 (CH), 128.2 (CH), 122.8 (C), 84.3 (C), 83.4 (C), 79.2 (C), 71.3 (CH), 19.9 (CH_2), 18.9 (CH_2); IR (neat): 2924, 2130, 1491, 1240, 1074, 745 cm^{-1}; MS (CI): *m/z* 185 ($[M-H]^+$, 69.7%), 153 (13.2%), 115 (100%); HRMS calcd for $C_{12}H_9S$ 185.0420; found 185.0421.

3.1.5. {3-[4,4-Dimethylpent-2-ynyl)thio]prop-1-ynyl}-benzene (18b). The title compound was prepared from γ-phenylpropargyl bromide and γ-*t*-butylpropargyl thioacetate[22] by the procedure mentioned above, and obtained in 75% yield as a yellowish oil, after separation by column chromatography (silica gel, ethyl acetate–hexane 5:95). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.46 (m, 2H), 7.30–7.32 (m, 3H), 3.65 (s, 2H), 3.48 (s, 2H), 1.25 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.7 (CH), 128.2 (CH), 128.1 (CH), 123.0 (C), 92.5 (C), 84.8 (C), 83.0 (C), 73.2 (C), 31.0 $(CH_3)_3$), 27.5 (C), 19.8 (CH_2), 19.7 (CH_2); IR (neat): 2195, 1490, 1361, 1266, 756, 690 cm^{-1}; MS (CI): *m/z* 243 (MH^+, 12.3%), 209 (21.5%), 115 (100%); HRMS calcd for $C_{16}H_{19}S$ 243.1207; found 243.1206.

3.1.6. [(1*E*)-3-(Prop-2-ynylthio)prop-1-enyl]benzene (31). The title compound was prepared from cinnamyl methanesulfonate and propargyl thioacetate, by the procedure described above, and obtained in 35% yield as colorless oil, after separation by column chromatography (silica gel, ethyl acetate–hexane 5:95). ^{1}H NMR (300 MHz, $CDCl_3$): 7.23–7.40 (m, 5H), 6.50 (br d, *J*=15.6 Hz, 1H), 6.15 (dt, *J*=15.6, 7.5 Hz, 1H), 3.46 (dd, *J*=7.5, 1.2 Hz, 2H),

3.19 (d, J=2.7 Hz, 2H), 2.27 (t, J=2.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 136.5 (C), 132.9 (CH), 128.5 (CH), 127.6 (CH), 126.3 (CH), 124.4 (CH), 78.0 (C), 71.1 (CH), 33.4 (CH_2), 17.8 (CH_2); MS (CI): m/z 189 (MH^+, 30.4%), 155 (6.2%), 117 (100%); HRMS calcd for $C_{12}H_{13}S$ 189.0738; found 189.0721.

3.1.7. 1,4-Bis-[3-(but-2-ynylsulfonyl)prop-1-ynyl]benzene (10b). To a magnetically stirred solution of bis-sulfide **10a** (1.0 g, 3.4 mmol) in methanol (20 mL) at 0°C was added a solution of 49.5% $KHSO_5$ (2.5 equiv.) in water (20 mL). The reaction mixture was stirred for six days at room temperature before it was diluted with water and extracted with chloroform. The organic layer was washed with water (3×100 mL), satd. NaCl and then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a mixture of products, which was separated by column chromatography (silica gel, ethyl acetate–hexane 1:1). The bis-sulfone product (0.63 g, 53%) was recrystallized from chloroform as yellowish crystals. Mp 194–195°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.58 (s, 4H), 4.72 (s, 4H), 4.53 (d, J=2.4 Hz, 4H), 3.64 (t, J=2.4 Hz, 2H); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 132.9 (CH), 122.9 (C), 86.7 (C), 80.9 (C), 79.7 (CH), 73.0 (C), 45.5 (CH_2), 44.8 (CH_2); IR (neat): 1320, 1121 cm^{-1}; MS (EI): m/z 358 (M^+, 42.6%), 294 (6.2%), 152 (100%); HRMS calcd for $C_{18}H_{14}O_4S_2$ 358.0334; found 358.0362.

3.1.8. 1,4-Bis-{3-[(4-methylpent-4-en-2-ynylsulfonyl)-prop-1-ynyl]}benzene (10d). The title compound was prepared from bis-sulfide **10c** and oxone reagent, according to the above procedure and recrystallized from hexane–chloroform as white crystals in 63% yield. Mp 115–121°C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (s, 4H), 5.41–5.42 (m, 2H), 5.36 (quintet, J=1.5 Hz, 2H), 4.29 (s, 4H), 4.20 (s, 4H), 1.92 (dd, J=1.5, 1 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 132.0 (CH), 125.4 (C), 124.4 (CH_2), 122.3 (C), 89.4 (C), 87.2 (C), 78.2 (C), 74.7 (C), 44.7 (CH_2), 44.4 (CH_2), 22.9 (CH_3); IR (neat): 1611, 1508, 1321, 1128 cm^{-1}; MS (CI): m/z 439 (MH^+, 27%), 375 (15.5%), 295 (66%), 231 (100%); HRMS calcd for $C_{24}H_{23}O_4S_2$ 439.1038; found 439.1012.

3.1.9. (4-Methylthien-3-yl){4-[(4-methylthien-3-yl)carbonyl]phenyl}methanone (14a). To a solution of bis-sulfide **10a** (1.0 g, 3.4 mmol) in acetonitrile (30 mL) was added DBU (2 mL, 13.6 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with dichloromethane (100 mL), washed with water (3×100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a mixture of two products **14a** and **15a**, which was separated by column chromatography (silica gel, ethyl acetate–hexane 1:1) as a colorless oil in 8% yield each. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (s, 4H), 7.71 (d, J=1.5 Hz, 2H), 7.28 (quintet, J=1.5 Hz, 2H), 2.53 (d, J=1 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 189.3 (C-q), 141.5 (C-q), 141.2 (C-q), 140.9 (C-q), 133.1 (CH), 129.1 (CH), 126.1 (CH), 15.2 (CH_3); IR (neat): 1643, 1455, 846, 723 cm^{-1}; MS (CI): m/z 326 (M^+, 100%), 310 (13%), 229 (14%), 125 (51.5%); HRMS calcd for $C_{18}H_{14}O_2S_2$ 326.0435; found 326.0430.

3.1.10. [4-(Hydroxymethyl)thien-3-yl]{4-[(4-methylthiene-3-yl)carbonyl]phenyl}methanone (15a). ^{1}H NMR (300 MHz, $CDCl_3$): δ; 7.93 (s, 2H), 7.91 (s, 2H), 7.87 (d, J=3 Hz, 1H), 7.72 (d, J=1.5 Hz, 1H), 7.38 (dt, J=3, 0.5 Hz, 1H), 7.28 (q, J=1 Hz, 1H), 4.75 (s, 2H), 2.54 (d, J=1 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 191.8 (C), 189.1 (C), 143.6 (C), 142.1 (C), 141.5 (C), 141.3 (C), 140.8 (C), 138.9 (C), 138.8 (CH), 133.2 (CH), 129.5 (CH), 129.2 (CH), 126.1 (CH), 125.6 (CH), 59.9 (CH_2), 15.2 (CH_3); IR (neat): 1657, 1645 cm^{-1}; MS (CI): m/z 342 (M^+, 78.6%), 325 (64.6%), 245 (10.6%) 203 (100%); HRMS calcd for $C_{18}H_{14}O_3S_2$ 342.0384; found 342.0390.

3.1.11. 6-Methyl-4-[4-(6-methyl-1,3-dihydro-2-benzothien 2,2-dioxide-4-yl)phenyl]-1,3-dihydro-2-benzothiophene 2,2-dioxide (13d). To a solution of bis-sulfone **10d** (1.49 g, 3.4 mmol) in DMSO (30 mL) was added Et_3N (1.9 mL, 13.6 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with dichloromethane (100 mL), washed with water (3×100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a crude product in 54% yield. The yellowish solid was purified by chromatography (silica gel, ethyl acetate) and then recrystallized from chloroform–hexane as white crystals. Mp 150–180°C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 4H), 7.22 (s, 2H), 7.16 (s, 2H), 4.42 (s, 4H), 4.35 (s, 4H), 2.44 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.4 (C), 139.2 (C), 131.9 (C), 130.4 (CH), 128.7 (CH), 126.5 (C), 125.9 (CH), 57.1 (CH_2), 56.4 (CH_2), 21.4 (CH_3); IR (KBr): 2977, 1697, 1490, 1384, 1064, 759 cm^{-1}; MS (CI): m/z 439 (MH^+, 100%), 375 (39.6%); HRMS calcd for $C_{24}H_{23}O_4S_2$ 439.1038; found 439.1020.

3.2. General procedure for the reaction of sulfur and selenium bridged di- and tetrapropargylic systems with *t*-BuOK

To a stirred solution of *t*-BuOK (1.0 equiv.) in dry THF (5 mL) was added in one portion a solution of the desired di- or tetrapropargylic compound (0.5 mmol) in 10 mL of dry THF. After the mixture was stirred for 1 min at room temperature, it was diluted with water–dichloromethane (40 mL, each) and the organic layer was washed with 3% HCl (2×50 mL), water (3×50 mL) and satd. NaCl (1×50 mL). The organic layer was dried over anhydrous $MgSO_4$ and solvent removed under reduced pressure. The data for all cyclization products are listed below.

3.2.1. 6-Methyl-4-[4-(6-methyl-4,5-dihydro-2-benzothien-4-yl)phenyl]-4,5-dihydro-2-benzothiophene (12c). The title compound was obtained from **10c** by the use of the general procedure in 36% yield as a yellowish viscous oil, after purification by column chromatography (silica gel, ethyl acetate–hexane 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (s, 4H), 6.86 (d, J=3 Hz, 2H), 6.53 (ddd, J=2.5, 1.5, 1 Hz, 2H), 6.36 (bs, 2H), 4.06 (ddd, J=11.5, 6.5, 1.5 Hz, 2H), 2.52 (bdd, J=16, 11.5 Hz, 2H), 2.43 (ddt, J=16, 6.5, 0.5 Hz, 2H), 1.89 (s, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 142.5 (C), 139.98 (C), 137.9 (C), 136.7 (C), 128.2 (CH), 120.0 (CH), 118.6 (CH), 116.7 (CH), 42.7 (CH), 38.7 (CH_2) 23.4 (CH_3); MS (CI): m/z; 374 (MH^+, 100%), 225 (34%), 149 (90.8%); HRMS calcd for $C_{24}H_{23}S_2$ 375.1241; found 375.1232.

Compounds **16a** and **17a** were obtained from **10a** by the

general procedure as inseparable mixture and purified by column chromatography (silica gel, hexane); colorless oil, total yield 42%.

3.2.2. 2-((*E*)-2-{4-[(*Z*)-2-Thien-2-ylvinyl]phenyl}vinyl)-thiophene (16a). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54–7.56 (m, 2H), 7.45 (dm, J=16.2 Hz, 1H), 7.37 (m, 2H), 7.36 (m, 1H), 7.27 (td, J=5.0, 1.5 Hz, 1H), 7.19 (dm, J=3.5 Hz, 1H), 7.06–7.08 (m, 1H), 7.05 (dd, J=5.0, 3.5 Hz, 1H), 7.00 (d, J=16.2 Hz, 1H), 6.94 (ddd, J=5.5, 3.5, 1.5 Hz, 1H), 6.76 (d, J=12.0 Hz, 1H), 6.57 (d, J=12.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.6 (C), 140.3 (C), 137.4 (C), 137.2 (C), 130.0 (CH), 129.4 (CH), 129.36 (CH), 129.2 (CH), 128.5 (CH), 128.4 (CH), 127.4 (CH), 127.2 (CH), 126.6 (CH), 125.5 (CH), 124.1 (CH), 122.9 (CH); IR (neat) (in mixture with **17a**): 1660, 1625, 1426, 1271, 1201, 957, 814, 690 cm^{-1}; MS (CI): m/z 295 (MH^+, 72%), 294 (100%); HRMS calcd for $C_{18}H_{15}S_2$ 295.0615; found 295.0616.

3.2.3. 2-((*Z*)-2-{4-[(*Z*)-2-Thien-2-ylvinyl]phenyl}vinyl)-thiophene (17a). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (s, 4H), 7.27 (td, J=5.0, 1.5 Hz, 2H), 7.04–7.09 (m, 2H), 6.94 (ddd, J=5.5, 3.5, 1.5 Hz, 2H), 6.78 (d, J=12.0 Hz, 2H), 6.60 (d, J=12.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.3 (C), 137.5 (C), 129.7 (CH), 129.5 (CH), 129.1 (CH), 127.2 (CH), 126.6 (CH), 124.3 (CH).

Compounds **19b** and **20b** were obtained from **18b** by the general procedure as inseparable mixture and purified by column chromatography (silica gel, hexane); colorless oil, total yield 21%.

3.2.4. 3-*t*-Butyl-2-[(*E*)-2-phenylvinyl]thiophene (19b). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J=15.5 Hz, 1H), 7.43–7.45 (m, 2H), 7.32–7.37 (m, 2H), 7.22–7.26 (m, 1H), 7.04 (d, J=5.0 Hz, 1H), 6.99 (d, J=5.0 Hz, 1H), 6.84 (d, J=15.5 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.2 (C), 137.4 (C), 136.0 (C), 128.7 (CH), 128.3 (CH), 127.8 (CH), 127.4 (CH), 126.3 (CH), 125.7 (CH), 122.5 (CH), 34.3 (C), 32.0 ($(CH_3)_3$); IR (neat) (in mixture with **20b**): 2927, 1681, 1491, 1462, 1448, 1363, 1263, 694 cm^{-1}; MS (CI): m/z 243 (MH^+, 100%); HRMS calcd for $C_{16}H_{19}S$ 243.1207; found 243.1209.

3.2.5. 3-*t*-Butyl-2-[(*Z*)-2-phenylvinyl]thiophene (20b). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16–7.21 (m, 5H), 7.07 (d, J=5 Hz, 1H), 7.00 (d, J=5 Hz, 1H), 6.81 (d, J=12 Hz, 1H), 6.58 (d, J=12 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.7 (C), 136.4 (C), 132.7 (C), 131.8 (CH), 129.4 (CH), 128.6 (CH), 128.1 (CH), 127.3 (CH), 123.4 (CH), 124.0 (CH), 34.3 (C), 31.1 (CH_3).

Compounds **21** and **22** were obtained from **1a** by the general procedure as inseparable mixture and purified by column chromatography (silica gel, hexane); colorless oil, total yield 22%.

3.2.6. 3-Phenyl-2-[(*E*)-2-phenylvinyl]thiophene (21). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43–7.45 (m, 2H), 7.33–7.42 (m, 7H), 7.29–7.33 (m, 1H), 7.27 (d, J=16 Hz, 1H), 7.21 (d, J=5 Hz, 1H), 7.09 (d, J=5 Hz, 1H), 6.99 (d, J=16 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.6 (C), 137.4 (C), 137.1 (C), 136.3 (C), 129.9 (CH), 129.1 (CH), [*o*, *m* and *p* of both isomers—129.3 (CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.39 (CH), 128.37 (CH), 128.36 (CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH)], 123.3 (CH), 121.2 (CH); MS (CI): m/z 263 (MH^+, 100%); HRMS calcd for $C_{18}H_{15}S$ 263.0816; found 263.0810.

3.2.7. 3-Phenyl-2-[(*Z*)-2-phenylvinyl]thiophene (22). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46–7.48 (m, 2H), 7.41–7.43 (m, 2H), 7.23–7.40 (m, 6H), 7.12 (d, J=5 Hz, 1H), 7.05 (d, J=5 Hz, 1H), 6.63 (d, J=12 Hz, 1H), 6.61 (d, J=12 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.7 (C), 137.0 (C), 136.3 (C), 134.2 (C), 130.4 (CH), [*o*, *m* and *p* of both isomers—129.3 (CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.39 (CH), 128.37 (CH), 128.36 (CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH)], 128.2 (CH), 124.7 (CH), 123.0 (CH).

Compounds **19c** and **20c** were obtained from **18c** by the general procedure as inseparable mixture and purified by column chromatography (silica gel, hexane); colorless oil, total yield 24%.

3.2.8. 3-Phenyl-2-[(*E*)-2-phenylvinyl]selenophene (19c). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J=5.5 Hz, 1H; $^2J_{Se-H}$=23.4 Hz), 7.43–7.46 (m, 2H), 7.41–7.42 (m, 2H), 7.39 (m, 2H), 7.36 (d, J=5.5 Hz, 1H), 7.32–7.34 (m, 1H), 7.29–7.31 (m, 2H), 7.26 (d, J=15.5 Hz, 1H), 7.22 (m, 1H), 6.88 (d, J=15.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.8 (C), 143.4 (C), 137.3 (C), 137.2 (C), 133.5 (CH), 130.5 (CH), 129.3 (CH), 128.7 (CH), 128.5 (CH), 127.6 (CH), 127.1 (CH), 127.2 (CH), 123.4 (CH); IR (neat) (in mixture with **20c**): 1645, 1597, 1487, 1446, 1252, 1066, 948, 700 cm^{-1}; MS (CI): m/z 306, 307, 308, 310, 312 (M^+, 1:1:3:7:1, 100%), 229 (46%); HRMS calcd for $C_{18}H_{14}^{80}Se$ 310.0250; found 310.0251.

3.2.9. 3-Phenyl-2-[(*Z*)-2-phenylvinyl]selenophene (20c). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, J=5.5 Hz, 1H; $^2J_{Se-H}$=22.5 Hz), 7.43–7.45 (m, 2H), 7.41–7.42 (m, 2H), 7.39–7.40 (m, 2H), 7.36–7.37 (m, 2H), 7.33–7.35 (m, 1H), 7.29–7.32 (m, 1H), 7.29 (d, J=5.5 Hz, 1H), 6.67 (d, J=12 Hz, 1H), 6.61 (d, J=12 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.5 (C), 139.4 (C), 136.8 (C), 131.6 (CH), 129.9 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 128.7 (CH), 128.3 (CH), 127.8 (CH), 127.1 (CH), 125.5 (CH).

Compounds **25**, **26** and **27** were obtained from **23b** by the general procedure and purified by column chromatography (silica gel, hexane).

3.2.10. 3-Isopropenyl-2-[(1*E*)-3-methylbuta-1,3-dienyl]-selenophene (25). Colorless oil; yield 3%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, J=5.7 Hz, 1H), 7.18 (d, J=5.7 Hz, 1H), 6.86 (d, J=15.7 Hz, 1H), 6.59 (d, J=15.7 Hz, 1H), 5.24 (dq, J=2.2, 1.5 Hz, 1H), 5.06 (dq, J=1.3, 0.8 Hz, 1H), 5.02 (quintet, J=1.0 Hz, 1H), 4.96 (dq, J=2.2, 1.0 Hz, 1H), 2.06 (dd, J=1.5, 1.0 Hz, 3H), 1.93 (dd, J=1.5, 0.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.1 (C), 143.3 (C), 142.1 (C), 140.8 (C), 132.8 (CH), 131.5 (CH), 126.7 (CH), 123.9 (CH), 116.8 (CH_2), 116.6 (CH_2), 24.0 (CH_3), 18.7 (CH_3).

3.2.11. 5a,7a-Dimethyl-5a,6,7,7a-tetrahydrocyclobuta-[3,4]benzo[1,2b]selenophene (26). Colorless oil; yield

23%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (dd, J=5.6, 0.6 Hz, 1H; $^2J_{Se-H}$=47.0 Hz), 7.17 (dd, J=5.6, 0.8 Hz, 1H; $^3J_{Se-H}$=9.2 Hz), 6.35 (dd, J=9.7, 0.8 Hz, 1H), 5.44 (dd, J=9.7, 0.6 Hz, 1H), 2.32 (ddd, J=11.0, 9.0, 6.3 Hz, 1H), 2.19 (ddd, J=10.8, 9.0, 6.2 Hz, 1H), 2.02 (ddd, J=11.0, 9.0, 6.3 Hz, 1H), 1.90 (ddd, J=10.8, 9.0, 6.2 Hz, 1H), 1.36 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.2 (C), 137.1 (C), 132.9 (CH), 129.1 (CH), 127.0 (CH), 119.7 (CH), 42.7 (C), 41.4 (C), 36.5 (CH_2), 35.0 (CH_2), 22.6 (CH_3), 22.5 (CH_3); MS (CI): *m/z* 234, 235, 236, 238, 240 (M^+, 1:1:3:7:1, 63%), 210 (100%), 197 (36%); HRMS calcd for $C_{12}H_{14}^{80}Se$ 238.0261; found 238.0280.

3.2.12. 7-Methyl-4-methylene-4,5,6,9-tetrahydrocycloocta[b]selenophene (27). Colorless oil; yield 4%; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, J=5.7 Hz, 1H), 7.16 (d, J=5.7 Hz, 1H), 5.57 (tq, J=7.0, 1.5 Hz, 1H), 5.09 (d, J=1.8 Hz, 1H), 4.98 (dt, J=1.8, 1.0 Hz, 1H), 3.56 (d, J=7.0 Hz, 2H), 2.58–2.59 (m, 2H), 2.36–2.40 (m, 2H), 1.63–1.70 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 133.5 (CH), 124.9 (CH), 121.6 (CH), 114.7 (CH_2), 34.8 (CH_2), 33.0 (CH_2), 29.7 (CH_2), 25.0 (CH_3); MS (CI): *m/z* 234, 235, 236, 238, 240 (M^+, 1:1:3:7:1, 35%), 223 (100%); HRMS calcd for $C_{12}H_{14}^{80}Se$ 238.0261; found 238.0290. Due to the small amount of this product, quaternary carbons are not observed.

3.2.13. 3-Methyl-4-phenyl-4*H*-thiopyran (32). The title compound was obtained from **31** by the use of the general procedure in 70% yield as yellowish oil, after purification by column chromatography (silica gel, ethyl acetate–hexane 5:200). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30–7.34 (m, 5H), 6.16 (ddd, J=10.0, 2.5, 1.2 Hz, 1H), 5.91 (dq, J=2.5, 1.2 Hz, 1H), 5.74 (dd, J=10.0, 5.1 Hz, 1H), 4.00 (d, J=5.1 Hz, 1H), 1.65 (dd, J=1.2, 0.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 128.8 (CH), 128.1 (CH), 126.9 (CH), 122.9 (CH), 115.8 (CH), 110.7 (CH), 45.9 (CH), 23.7 (CH_3); MS (CI): *m/z* 189 (MH^+, 100%), 157 (19.3%), 111 (93.7%); HRMS calcd for $C_{12}H_{13}S$ 189.0738; found 189.0734.

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