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NEW APPLICATIONS OF HETARYL THIOKETONES FOR THE SYNTHESIS OF HETARYL-SUBSTITUTED ETHENES VIA 'TWO-FOLD EXTRUSION REACTION'

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Dedicated to Professor Dr. Lutz F. Tietze, University of Göttingen (Germany), on the occasion of his 75th birthday

Abstract – A series of aryl/hetaryl thioketones was applied for the reactions with aryl/hetaryldiazomethanes yielding, after elimination of N_2, the corresponding thiiranes. The relatively unstable dihetaryldiazomethanes were generated in situ from the corresponding hydrazones by oxidation with DMSO. The obtained thiiranes were converted into tetraaryl/hetaryl-substituted ethenes in good yields by desulfurization performed with tris(diethylamino)phosphine ($(Et_2N)_3P$).

INTRODUCTION

Hetaryl-substituted ethenes constitute a class of organic compounds with great importance for applications in materials chemistry. The most relevant usage relates to their optoelectronic properties and crystal engineering.[1] They also display unique electrochemical properties, and as electron donors they were used for the synthesis of stable dications.[2] In addition, they are precursors of polyaromatic heterocycles, which can be prepared via photochemically induced oxidative cyclizations.[3]

The synthesis of symmetrical aryl/hetaryl-substituted ethenes is based on the McMurry protocol, in which the corresponding aryl/hetaryl ketones are treated with $TiCl_4$, Zn dust, and pyridine in boiling THF.[3,4]

Recently, another method was reported, in which non-symmetrical ethenes are accessible. In that case, an aryl/hetaryl ketone is initially converted to the corresponding *gem*-dibromoethene, which subsequently undergoes reaction with arene/hetarene via Suzuki-Stille coupling, leading to tetraaryl/hetaryl-substituted ethenes in decent yields.[1]

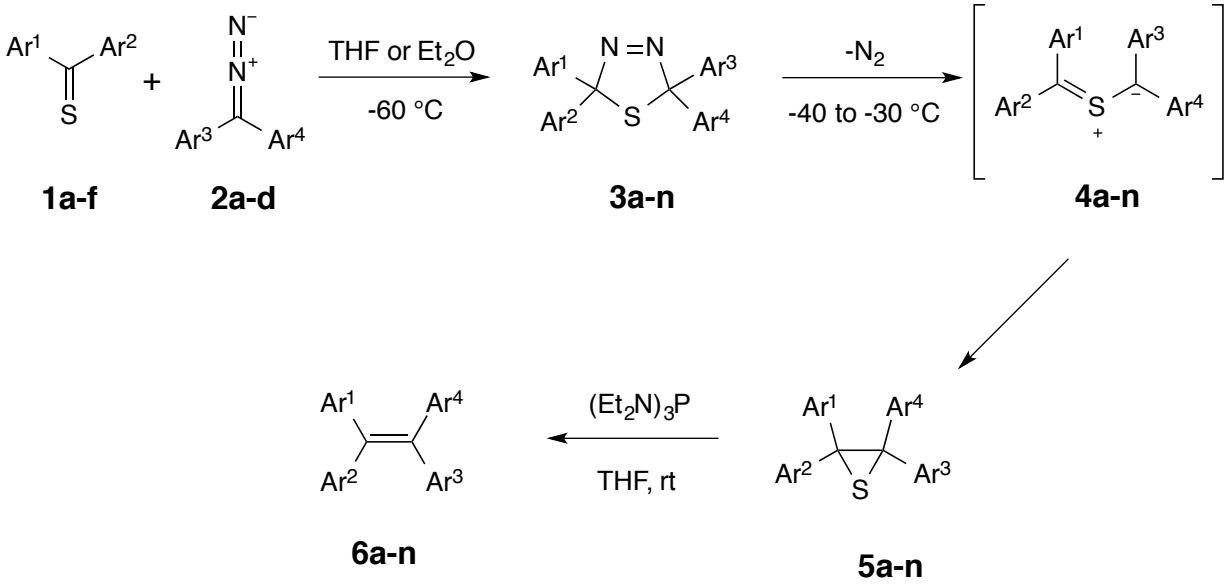
Another well-known method for the synthesis of differently substituted ethenes is the desulfurization of thiiranes, which in turn can easily be prepared according to the Eschenmoser protocol (Eschenmoser sulfide contraction)[5] or by treatment of thioketones with the corresponding diazo compounds. In the latter case, diaryl thioketones react with diaryldiazomethanes with spontaneous elimination of N_2 to give thiiranes as exclusive products.[6] The subsequent desulfurization can be efficiently achieved using P(III)-compounds such as Ph_3P or $(Et_2N)_3P$. This stepwise procedure is known as 'two-fold extrusion reaction'.[6a,7]

In a recent publication we described a convenient method for the preparation of diaryl/hetaryl thioketones containing furan-2-yl, thiophen-2-yl, or selenophen-2-yl substituents.[8] They were shown to react vigorously with diazomethane even at low temperature affording 4,4,5,5-tetrasubstituted 1,3-dithiolanes via a proposed diradical mechanism.[8,9]

The goal of the present study was the examination of the reaction of aryl/hetaryl thioketones with aryl/hetaryldiazomethanes as a possible route to tetraaryl/hetaryl thiiranes, which subsequently could be desulfurized to yield the corresponding tetrasubstituted ethene derivatives.

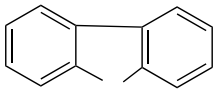
RESULTS AND DISCUSSION

The reactions of aryl/hetaryl thioketones **1a**-**f** with aryl/hetaryldiazomethanes **2a**-**d** were performed at –60 °C to room temperature over night. Whereas diphenyldiazomethane (**2a**) and diazofluorenone (**2b**) can be prepared, stored, and used in syntheses, the hitherto unknown (phenylthiophen-2-yl)diazomethane (**2c**) and di(thiophen-2-yl)diazomethane (**2d**) were prepared in situ and used without isolation, because they decompose rapidly at room temperature. The disappearance of the characteristic color of the thioketones **1** was observed between –40 and –30 °C, accompanied with the evolution of N_2. The crude mixtures were purified by column chromatography (SiO_2) leading to a single product in each case. The structures of the expected thiiranes **5** (Scheme, Table) were proved on the basis of their spectroscopic data and elemental analyses. For example, in the ^{13}C-NMR spectrum of **5a**, the characteristic signals of C(2) and C(3) were observed at 62.3 and 67.3 ppm, and in the case of **5d** the analogous signals appeared at 56.0 and 69.0 ppm. In the symmetrical tetra(thiophen-2-yl)thiirane (**5k**), the signal for C(2) and C(3) was found at 57.8 ppm. The formation of 1,2-diphenyl-1,2-di(thiophen-2-yl)thiirane (**5i**) occurred with low selectivity leading to a ca. 1:1.3-mixture of two stereoisomers (*cis*/*trans*), which could not be separated by column chromatography.



Scheme

Table. Synthesis of thiiranes **5** and ethene derivatives **6**[a])

1	Ar^1	Ar^2	**2**	Ar^3	Ar^4	**5**	Yield (%)[b])	**6**	Yield (%)[c])
a	Ph	Thi	**a**	Ph	Ph	**a**	44.6	**a**[10]	56.0
b	Ph	Sel	**a**	Ph	Ph	**b**	42.0	**b**	36.8
c	Fur	Fur	**a**	Ph	Ph	**c**	45.6	**c**	74.0
d	Thi	Thi	**a**	Ph	Ph	**d**	57.2	**d**[3]	68.8
e	Sel	Sel	**a**	Ph	Ph	**e**	-	**e**	71.0[d])
f	Fur	Thi	**a**	Ph	Ph	**f**	48.0	**f**	76.8
a	Ph	Thi	**b**			**g**	67.4	**g**	61.6
b	Ph	Sel	**b**			**h**	41.4	**h**	65.0
a	Ph	Thi	**c**	Ph	Thi	**i**	46.0[e])	**i**[4]	86.1[f])
a	Ph	Thi	**d**	Thi	Thi	**j**	35.1	**j**	23.4
d	Thi	Thi	**d**	Thi	Thi	**k**	11.6	**k**	[g])
e	Sel	Sel	**d**	Thi	Thi	**l**	56.2	**l**	37.6
f	Fur	Thi	**d**	Thi	Thi	**m**	72.4	**m**	73.5
e	Sel	Sel	**c**	Ph	Thi	**n**	68.9	**n**	68.9

[a]) For reaction conditions see Scheme; Abbreviations: Ph = Phenyl, Fur = Furan-2-yl, Thi = Thiophen-2-yl, Sel = Selenophen-2-yl. [b]) With respect to starting thioketone **1**. [c]) With respect to thiirane **5**. [d]) With respect to thioketone **1e**. [e]) *Cis*/*trans*-mixture (ca. 1:1). [f]) (*Z*/*E*)-mixture (ca. 1:1.3). [g]) Not prepared (see ref. [2a]).

In general, the thiiranes **5** are fairly stable compounds, which were isolated in ca. 40 – 70% yield. Only in the case of 2,2-diphenyl-3,3-di(selenophen-2-yl)thiirane (**5e**), the crude product was identified as a mixture of **5e** and the corresponding ethene **6e**, which apparently was formed via spontaneous extrusion of sulfur. The chromatographic separation of both compounds was unsuccessful, and for that reason, the crude product was desulfurized by treatment with $(Et_2N)_3P$ in THF solution. The analogous method was applied for the removal of the S-atom from thiiranes **5** to give the corresponding ethenes **6** in yields up to 86% (Scheme, Table). Their structures were confirmed by spectroscopic data and elemental analyses. The desulfurization of the *cis*/*trans*-mixture of **5i** gave a mixture of the (*Z*/*E*)-isomers of 1,2-diphenyl-1,2-di(thiophen-2-yl)ethene (**6i**).

The mechanism of the reaction of thioketones **1** with diazo compounds **2** is presented in the Scheme and corresponds to the interpretation of the so-called 'Schönberg reaction'.[11] The diaryldiazomethane **2** reacts as a 1,3-dipole with the C=S group as the dipolarophile in a [3+2] cycloaddition to yield the unstable 2,2,5,5-tetraaryl-2,5-dihydro-1,3,4-thiadiazole **3**, which easily eliminates N_2 even below 0 °C. The intermediate thiocarbonyl ylide **4** undergoes a 1,3-dipolar electrocyclization to give thiirane **5** as the exclusive product. It is well known that the reactive tetraaryl-substituted thiocarbonyl ylides do not undergo the competitive reactions leading to other products like 1,4-dithianes (dimerization) or 1,3-dithiolanes ([3+2] cycloadditions with starting thioketones).

CONCLUSIONS

The present study showed that the easily accessible aryl/hetaryl thioketones react smoothly with aryl/hetaryldiazomethanes and, after spontaneous elimination of N_2, the corresponding thiiranes are obtained as products of the 1,3-dipolar electrocyclization of the intermediate reactive thiocarbonyl ylides. In general, the thiiranes are stable compounds and can be isolated as pure substances. The subsequent desulfurization can be efficiently achieved by their treatment with tris(diethylamino)phosphine. This method, corresponding to the 'two-fold extrusion' protocol, is performed without any metal catalyst and can be considered as an attractive alternative approach to polyhetaryl-substituted ethenes. Moreover, in contrast to the McMurry approach, it allows the preparation of non-symmetrical ethene derivatives, and the substitution pattern can be designed by the selection of the aryl/hetaryl thioketone and the aryl/hetaryl-diazomethane.

EXPERIMENTAL

General remarks. Melting points were determined in a capillary using a Melt-Temp. II (Aldrich) apparatus, and they are uncorrected. The IR spectra were recorded on a NEXUS FT-IR spectrophotometer in KBr; absorptions in cm^{-1}. The ^1H- and $^{13}C\{^1H\}$-NMR spectra were measured on a Bruker Avance III

instrument (600 and 150 MHz, resp.) using solvent signals as reference. Chemical shifts (δ) are given in ppm and coupling constants *J* in Hz. ESI-MS and CI-MS were recorded on a Varian 500-MS LC IonTrap spectrometer in the Laboratory of Mass Spectrometry of the University of Łódź; the HR-ESI-MS for **6j** was recorded on a Bruker maxis spectrometer in the Laboratory of Mass Spectrometry of the University of Zurich. Elemental analyses were performed in the Laboratory of the Faculty of Chemistry (University of Łódź).

Starting materials. Hetaryl thioketones **1** were obtained in a typical manner from the corresponding ketones and Lawesson's reagent in boiling toluene or benzene.[12] Aromatic and heteroaromatic hydrazones, as starting materials for the preparation of the aryl/hetaryldiazomethanes, were prepared from the corresponding ketones by treatment with excess hydrazine hydrate in EtOH according to the published procedure for benzophenone hydrazone.[13] Diphenyldiazomethane (**2a**) was prepared and separated as a red oil that solidified on cooling according to the described procedure via dehydrogenation of hydrazones with activated DMSO in the presence of Et_3N.[14] Heteroaromatic diazo compounds were prepared *in situ* according to the same procedure. 9-Diazofluorene[15] was obtained in a typical manner from corresponding hydrazone and yellow mercury oxide.

General procedure for the reaction of hetaryl thioketones 1 with in situ generated diazo compounds 2. A solution of 1 mmol of the corresponding thioketone **1** in 1 mL of dry Et_2O was cooled in a acetone/dry ice bath to –60 °C. The mixture was treated with a cooled solution containing excess of the corresponding freshly prepared diazo compound **2**. The mixture was stirred magnetically and allowed to warm to room temperature. Change of the color of the solution was observed at ca. –40 to –30 °C depending on the used thioketone **1**. The solvent was evaporated and the residue was purified chromatographically (SiO_2) using mixtures of hexane and CH_2Cl_2 as eluent. The obtained products were additionally purified by crystallization from hexane or petroleum ether containing a small amount of CH_2Cl_2.

2-(2,3,3-Triphenylthiiran-2-yl)thiophene (**5a**). Yield: 165 mg (44.6%). Mp 158.5–162.3 °C (hexane). ^{1}H-NMR: 6.55 (*dd*, $J_{H,H}$ = 3.7, 1.3 Hz, $1CH_{arom}$); 6.67 (*dd*, $J_{H,H}$ = 5.2, 3.8 Hz, $1CH_{arom}$); 6.97–6.99 (*m*, $4CH_{arom}$); 7.12–7.13 (*m*, $5CH_{arom}$); 7.20–7.21 (*m*, $3CH_{arom}$); 7.33–7.34 (*m*, $2CH_{arom}$); 7.39–7.41 (*m*, $2CH_{arom}$). ^{13}C-NMR: 62.3, 67.3 ($2C_q$); 126.1, 126.4, 126.7, 127.0, 127.1, 127.2, 127.3, 127.4, 128.6, 129.8, 130.9, 131.4 (12 signals for $18CH_{arom}$); 139.7, 139.8, 140.4, 148.5 ($4C_{arom}$). IR (KBr): 3057*m*, 3024*m*, 1600*m*, 1492*s*, 1444*s*, 1234*s*, 1077*m*, 833*m*, 750*s*, 697*vs*, 637*m*. CI-MS: 394 ($[M+1+Na]^+$, 18), 371 ($[M+1]^+$, 27), 370 (M^+, 13), 338 ($[M–S]^+$, 25), 337 ($[M–1–S]^+$, 100). Anal. Calcd for $C_{24}H_{18}S_2$ (370.08): C

77.79, H 4.89, S 17.31. Found: C 78.07, H 4.87, S 17.28.

2,2,3-Triphenyl-3-(selenophen-2-yl)thiirane (**5b**). Yield: 175 mg (42.0%). Mp 146.9–149.3 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.72 (*d*, $J_{H,H}$ = 3.8 Hz, 1CH_{arom}); 6.96 (*t*, $J_{H,H}$ = 5.6 Hz, 1CH_{arom}); 7.00–7.02 (*m*, 3CH_{arom}); 7.16–7.17 (*m*, 5CH_{arom}); 7.25–7.27 (*m*, 3CH_{arom}); 7.37 (*dd*, $J_{H,H}$ = 5.7, 1.9 Hz, 2CH_{arom}); 7.48–7.49 (*m*, 2CH_{arom}); 7.74 (*d*, $J_{H,H}$ = 5.7 Hz, 1CH_{arom}). ^{13}C-NMR: 64.4, 67.5 (2C_q); 126.4, 126.7, 127.0, 127.1, 127.2, 127.3, 127.5, 127.6, 127.7, 129.2, 129.7, 130.4, 130.8, 131.3, 131.7, 132.3 (16 signals for 18CH_{arom}); 139.7, 140.0, 140.4, 156.6 (4C_{arom}). IR (KBr): 3049*m*, 3023*m*, 1599*m*, 1490*s*, 1444*s*, 1233*s*, 1079*m*, 1029*m*, 834*m*, 777*s*, 742*s*, 700*vs*, 688*vs*, 658*m*. CI-MS: 419 [(M+2)$^+$, 100]], 418 [(M+1)$^+$, 15], 417 (M^+, 50)]. Anal. Calcd for $C_{24}H_{18}SSe$ (417.42): C 69.06, H 4.35, S 7.68. Found: C 69.36, H 4.33, S 7.57.

2-[2-(2-Furyl)-3,3-diphenylthiiran-2-yl]furan (**5c**). Yield: 157 mg (45.6%). Mp 128.6–130.8 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.06 (*dd*, $J_{H,H}$ = 3.4, 1.0 Hz, 2CH_{arom}); 6.16 (*dd*, $J_{H,H}$ = 3.4, 1.9 Hz, 2CH_{arom}); 7.14–7.18 (*m*, 6CH_{arom}); 7.25 (*dd*, $J_{H,H}$ = 1.9, 1.0 Hz, 2CH_{arom}); 7.38–7.40 (*m*, 4CH_{arom}). ^{13}C-NMR: 49.9, 67.1 (2C_q); 110.3, 111.0, 127.0, 127.5, 129.5, 142.3 (6 signals for 16CH_{arom}); 140.4, 151.2 (2 signals for 4C_{arom}). IR (KBr): 3083*m*, 3057*m*, 3030*m*, 1598*m*, 1585*m*, 1489*s*, 1445*s*, 1221*m*, 1198*m*, 1149*s*, 1081*m*, 1066*m*, 1013*vs*, 930*m*, 852*m*, 817*m*, 741*vs*, 701*vs*, 647*m*. CI-MS: 367 (25, [M+Na]$^+$), 345 (73, [M+1]$^+$), 344 (52, M^+), 312 (29, [M–S]$^+$), 311 (100, [M–1–S]$^+$). Anal. Calcd for $C_{22}H_{16}O_2S$ (344.43): C 76.72, H 4.68, S 9.31. Found: C 76.70, H 4.70, S 9.25.

2-[3,3-Diphenyl-2-(2-thienyl)thiiran-2-yl]thiophene (**5d**). Yield: 215 mg (57.2%). Mp 148.5–150.1 °C (petroleum ether). ^{1}H-NMR: 6.74 (*dd*, $J_{H,H}$ = 5.0, 3.5 Hz, 2CH_{arom}); 6.82 (*dd*, $J_{H,H}$ = 3.6, 1.2 Hz, 2CH_{arom}); 7.07 (*dd*, $J_{H,H}$ = 5.0, 1.2 Hz, 2CH_{arom}); 7.13–7.18 (*m*, 6CH_{arom}); 7.35–7.38 (*m*, 4CH_{arom}). ^{13}C-NMR: 56.0, 69.0 (2C_q); 125.8, 126.1, 127.0, 127.3, 128.9, 130.3 (6 signals for 16CH_{arom}); 139.9, 145.8 (2 signals for 4C_{arom}). IR (KBr): 3080*m*, 3059*m*, 3028*m*, 1599*m*, 1490*s*, 1444*s*, 1232*m*, 1080*m*, 1066*m*, 1033*m*, 854*m*, 822*m*, 752*m*, 697*vs*, 647*m*. Anal. Calcd for $C_{22}H_{16}S_3$ (376.56): C 70.17, H 4.28, S 25.55. Found: C 69.95, H 4.39, S 25.01.

2,2-Diphenyl-3,3-di(selenophen-2-yl)thiirane (**5e**). This product was detected in the crude reaction mixture together with **6e** and, without separation, was converted directly into alkene derivative **6e**. ^{1}H-NMR: 7.76 (*d*, $J_{H,H}$ = 1.3 Hz, 1CH_{arom}), 7.78 (*d*, $J_{H,H}$ = 1.3 Hz, 1CH_{arom}).

2-[3,3-Diphenyl-2-(2-thienyl)thiiran-2-yl]furan (**5f**). Yield: 173 mg (48.0%). Mp 126.4–128.3 °C

(petroleum ether/CH_2Cl_2). ^{1}H-NMR: 6.03 (*d*, $J_{H,H}$ = 3.2 Hz, 1CH_{arom}); 6.13 (*dd*, $J_{H,H}$ = 3.2, 1.9 Hz, 1CH_{arom}); 6.78 (*dd*, $J_{H,H}$ = 5.0, 3.6 Hz, 1CH_{arom}); 6.99 (*dd*, $J_{H,H}$ = 3.6, 1.0 Hz, 1CH_{arom}); 7.05 (*dd*, $J_{H,H}$ = 5.0, 1.0 Hz, 1CH_{arom}); 7.12–7.18 (*m*, 6CH_{arom}); 7.30 (*brs*, 1CH_{arom}); 7.38–7.41 (*m*, 4CH_{arom}). ^{13}C-NMR: 52.9, 68.9 (2C_q); 110.2, 110.9, 125.9, 126.4, 126.9, 127.0, 127.4, 127.8, 128.8, 129.5, 130.2, 142.3 (12 signals for 16CH_{arom}); 140.0, 140.6, 143.5, 152.7 (4C_{arom}). IR (KBr): 3082*m*, 3029*m*, 2999*m*, 2958*m*, 1596*m*, 1489*s*, 1445*s*, 1372*m*, 1233*m*, 1149*s*, 1070*m*, 1033*m*, 1010*s*, 944*m*, 850*m*, 813*m*, 787*m*, 735*vs*, 700*vs*, 648*m*. CI-MS: 383 (100, [*M*+Na]$^+$), 360 (17, M^+), 359 (39, [*M*–1]$^+$). Anal. Calcd for $C_{22}H_{16}OS_2$ (360.49): C 73.30, H 4.47, S 17.79. Found: C 73.04, H 4.51, S 17.42.

3'-Phenyl-3'-(2-thienyl)spiro[fluorene-9,2'-thiirane] (**5g**). Yield: 248 mg (67.4%). Mp 136.2–138.2 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.15 (*d*, $J_{H,H}$ = 7.7 Hz, 1CH_{arom}); 6.64 (*d*, $J_{H,H}$ = 7.7 Hz, 1CH_{arom}); 6.85–6.89 (*m*, 2CH_{arom}); 7.00 (*t*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}); 7.08 (*d*, $J_{H,H}$ = 3.5 Hz, 1CH_{arom}); 7.16 (*d*, $J_{H,H}$ = 5.00 Hz, 1CH_{arom}); 7.23 (*brs*, 3CH_{arom}); 7.28–7.31 (*m*, 2CH_{arom}); 7.36 (*t*, $J_{H,H}$ = 7.5 Hz, 2CH_{arom}); 7.75 (*d*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}); 7.77 (*d*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}). ^{13}C-NMR: 59.3, 59.6 (2C_q); 119.6, 119.7, 124.8, 125.6, 125.9, 126.2, 126.3, 126.6, 127.5, 127.9, 128.1, 128.4 (12 signals for 16CH_{arom}); 141.0, 141.1, 142.1, 142.6, 142.7, 147.1 (6C_{arom}). IR (KBr): 3061*m*, 3021*m*, 1578*m*, 1488*m*, 1447*s*, 1347*m*, 1299*m*, 1155*m*, 1076*m*, 1026*m*, 868*m*, 735*vs*, 697*vs*, 654*m*. Anal. Calcd for $C_{24}H_{16}S_2$ (368.51): C 78.22, H 4.38, S 17.40. Found: C 78.02, H 4.51, S 16.96.

3'-Phenyl-3'-(selenophen-2-yl)spiro[fluorene-9,2'-thiirane] (**5h**). Yield: 172 mg (41.4%). Mp 144.8–147.7 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.12 (*d*, $J_{H,H}$ = 7.8 Hz, 1CH_{arom}); 6.77 (*d*, $J_{H,H}$ = 7.8 Hz, 1CH_{arom}); 6.84 (*t*, $J_{H,H}$ = 7.6 Hz 1CH_{arom}); 6.99 (*t*, $J_{H,H}$ = 7.6 Hz 1CH_{arom}); 7.06–7.08 (*m*, 1CH_{arom}); 7.19–7.21 (*m*, 2CH_{arom}); 7.24–7.27 (*m*, 4CH_{arom}); 7.32 (*t*, $J_{H,H}$ = 7.4 Hz, 2CH_{arom}); 7.70 (*d*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}); 7.73 (*d*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}); 7.84 (*d*, $J_{H,H}$ = 5.6 Hz, 1CH_{arom}). ^{13}C-NMR: 59.8, 61.6 (2C_q); 119.6, 119.7, 125.2, 126.0, 126.3, 126.6, 127.5, 128.1, 128.4, 128.5, 130.0, 131.9 (12 signals for 16CH_{arom}); 141.0, 141.2, 142.4, 142.6, 142.7, 154.6 (6C_{arom}). IR (KBr): 3051*m*, 3019*m*, 1578*m*, 1488*m*, 1447*s*, 1155*m*, 1108*m*, 1004*m*, 834*m*, 728*vs*, 690*s*, 653*m*. Anal. Calcd for $C_{24}H_{16}SSe$ (415.41): C 69.36, H 3.88, S 7.72. Found: C 69.20, H 3.90, S 7.69.

2-[2,3-Diphenyl-3-(2-thienyl)thiiran-2-yl]thiophene (**5i**; mixture of *cis*/*trans*-isomers). Yield: 173 mg (46.0%). Mp 178.5–180.7 °C (hexane). ^{1}H-NMR: 6.54 (*dd*, $J_{H,H}$ = 3.6, 1.1 Hz, 1CH_{arom}); 6.66 (*dd*, $J_{H,H}$ = 5.2, 3.6 Hz, 1CH_{arom}); 6.81–6.84 (*m*, 2CH_{arom}); 6.98 (*dd*, $J_{H,H}$ = 5.1, 1.2 Hz, 1CH_{arom}); 7.08–7.11 (*m*, 3CH_{arom}); 7.16 (*dd*, $J_{H,H}$ = 5.1, 1.4 Hz, 1CH_{arom}); 7.27–7.31 (*m*, 5CH_{arom}); 7.51–7.53 (*m*, 2CH_{arom}). ^{13}C-NMR: 62.4, 62.9 (2C_q); 126.1, 126.3, 126.4, 127.2, 127.4, 127.5, 127.6, 128.5, 129.1, 130.1, 130.8

(12 signals for 16CH_{arom}); 139.3, 139.9, 146.4, 147.9 (4C_{arom}). IR (KBr): 3067*m*, 3024*m*, 1596*m*, 1490*m*, 1444*s*, 1428*m*, 1349*m*, 1231*m*, 1155*m*, 1076*m*, 1048*m*, 855*m*, 751*s*, 696*vs*, 614*m*. Anal. Calcd for $C_{22}H_{16}S_3$ (376.56): C 70.17, H 4.28, S 25.55. Found: C 69.86, H 4.21, S 25.74.

2-[2-Phenyl-3,3-bis(2-thienyl)thiiran-2-yl]thiophene (**5j**). Yield: 134 mg (35.1%). Mp 156.8–161.4 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.64–6.66 (*m*, 3CH_{arom}); 6.70 (*dd*, $J_{H,H}$ = 5.0, 3.7 Hz, 1CH_{arom}); 6.83 (*dd*, $J_{H,H}$ = 5.2, 3.7 Hz, 1CH_{arom}); 6.96 (*dd*, $J_{H,H}$ = 4.8, 1.6 Hz, 1CH_{arom}); 7.00 (*dd*, $J_{H,H}$ = 3.6, 1.3 Hz, 1CH_{arom}); 7.04 (*dd*, $J_{H,H}$ = 5.0, 1.1 Hz, 1CH_{arom}); 7.17–7.22 (*m*, 4CH_{arom}); 7.41–7.43 (*m*, 2CH_{arom}). ^{13}C-NMR: 56.7, 64.0 (2C_q); 125.9, 126.0, 126.3, 126.4, 126.5, 126.6, 127.6, 128.5, 128.7, 129.5, 130.6 (11 signals for 14CH_{arom}); 139.6, 144.2, 146.8, 147.1 (4C_{arom}). IR (KBr): 3098*m*, 3061*m*, 3024*m*, 1597*m*, 1489*m*, 1443*m*, 1428*m*, 1350*m*, 1229*s*, 1174*m*, 1073*m*, 1048*m*, 833*m*, 753*m*, 702*vs*, 616*m*. Anal. Calcd for $C_{20}H_{14}S_4$ (382.58): C 62.79, H 3.69, S 33.52. Found: C 62.37, H 3.78, S 33.40.

2-[2,3,3-Tris(2-thienyl)thiiran-2-yl]thiophene (**5k**). Yield: 45 mg (11.6%). Mp 150.9–153.2 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.75 (*dd*, $J_{H,H}$ = 5.0, 3.6 Hz, 4CH_{arom}); 6.86 (*dd*, $J_{H,H}$ = 3.6, 1.1 Hz, 4CH_{arom}); 7.10 (*dd*, $J_{H,H}$ = 5.0, 1.1 Hz, 4CH_{arom}). ^{13}C-NMR: 57.8 (2C_q); 126.2, 129.0 (2 signals for 12CH_{arom}); 144.9 (4C_{arom}). IR (KBr): 3098*m*, 3061*m*, 1488*m*, 1426*m*, 1349*m*, 1232*s*, 1077*m*, 1046*m*, 1005*m*, 854*m*, 832*m*, 811*m*, 796*m*, 700*vs*, 618*m*. Anal. Calcd for $C_{18}H_{12}S_5$ (388.61): C 55.63, H 3.11, S 41.26. Found: C 55.74, H 3.31, S 41.31.

2-[3,3-Di(selenophen-2-yl)-2-(2-thienyl)thiiran-2-yl]thiophene (**5l**). Yield: 271 mg (56.2%). Mp 143.1–144.4 °C (petroleum ether/CH_2Cl_2). ^{1}H-NMR: 6.79 (*dd*, $J_{H,H}$ = 5.2, 3.1 Hz, 2CH_{arom}); 6.94 (*dd*, $J_{H,H}$ = 3.7, 1.3 Hz, 2CH_{arom}); 7.02 (*dd*, $J_{H,H}$ = 5.6, 3.7 Hz, 2CH_{arom}); 7.09 (*dd*, $J_{H,H}$ = 3.7, 1.2 Hz, 2CH_{arom}); 7.14 (*dd*, $J_{H,H}$ = 5.2, 1.1 Hz, 2CH_{arom}); 7.83 (*dd*, $J_{H,H}$ = 5.6, 1.2 Hz, 2CH_{arom}). ^{13}C-NMR: 58.3, 62.0 (2C_q); 126.3, 128.8, 129.3, 131.3, 132.5 (5 signals for 12CH_{arom}); 145.0, 152.4 (2 signals for 4C_{arom}). IR (KBr): 3092*m*, 3077*m*, 1636*m*, 1445*m*, 1496*m*, 1430*m*, 1352*m*, 1235*s*, 1187*m*, 1122*m*, 1032*s*, 837*m*, 809*m*, 742*vs*, 691*vs*, 602*m*. Anal. Calcd for $C_{18}H_{12}S_3Se_2$ (482.40): C 44.82, H 2.51, S 19.94. Found: C 44.89, H 2.59, S 19.94.

2-[2,3,3-Tris(2-thienyl)thiiran-2-yl]furan (**5m**). Yield: 262 mg (72.4%). Mp 149.3–151.9 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.16 (*dd*, $J_{H,H}$ = 3.1, 0.7 Hz, 1CH_{arom}); 6.21 (*dd*, $J_{H,H}$ = 3.5, 1.9 Hz, 1CH_{arom}); 6.78–6.83 (*m*, 3CH_{arom}); 6.92–6.94 (*m*, 2CH_{arom}); 7.00 (*dd*, $J_{H,H}$ = 3.6, 1.2 Hz, 1CH_{arom}); 7.13–7.15 (*m*, 3CH_{arom}); 7.32 (*dd*, $J_{H,H}$ = 1.9, 0.7 Hz, 1CH_{arom}). ^{13}C-NMR: 54.7, 56.8 (2C_q); 110.4, 111.0, 126.0, 126.1, 126.2, 126.3, 126.4, 126.5, 128.2, 129.0, 129.1, 142.5 (12CH_{arom}); 142.7, 144.2, 145.0, 151.9 (4C_{arom}). IR (KBr): 3100*m*, 3063*m*, 1688*m*, 1608*m*, 1496*m*, 1428*m*, 1350*m*, 1232*s*, 1157*m*, 1139*m*, 1076*m*, 1041*m*,

1006*m*, 855*s*, 834*m*, 741*s*, 701*vs*, 613*m*. Anal. Calcd for $C_{18}H_{12}OS_4$ (372.55): C 58.03, H 3.25, S 34.43. Found: C 57.80, H 3.28, S 34.52.

2-[2-Phenyl-3,3-di(selenophen-2-yl)thiiran-2-yl]thiophene (**5n**). Yield: 328 mg (68.9%). Mp 162.4–164.1 °C (petroleum ether/CH_2Cl_2). ^{1}H-NMR: 6.72–6.73 (*m*, 2CH_{arom}); 6.89 (*dd*, $J_{H,H}$ = 4.0, 1.3 Hz, 1CH_{arom}); 6.94 (*dd*, $J_{H,H}$ = 5.6, 4.0 Hz, 1CH_{arom}); 7.08–7.11 (*m* 2CH_{arom}); 7.22–7.27 (*m*, 4CH_{arom}); 7.47–7.49 (*m*, 2CH_{arom}); 7.72 (*dd*, $J_{H,H}$ = 5.6, 1.1 Hz, 1CH_{arom}); 7.93 (*dd*, $J_{H,H}$ = 5.6, 1.1 Hz, 1CH_{arom}). ^{13}C-NMR: 60.8, 64.5 (2C_q); 126.6, 126.7, 127.6, 127.7, 128.4, 128.9, 129.1, 130.6, 130.7, 131.9, 132.1, 132.5 (12 signals for 14CH_{arom}); 139.8, 147.1, 151.6, 156.6 (4C_{arom}). IR (KBr): 3068*m*, 3027*m*, 1598*m*, 1489*s*, 1490*m*, 1443*s*, 1349*m*, 1230*s*, 1076*m*, 1032*m*, 841*m*, 805*m*, 751*m*, 688*vs*, 655*m*, 644*m*. Anal. Calcd for $C_{20}H_{14}S_2Se_2$ (476.38): C 50.43, H 2.96, S 13.46. Found: C 50.12, H 3.05, S 13.59.

General procedure for the desulfurization of thiiranes 5. Desulfurization of thiiranes **5** by treatment with tris(diethylamino)phosphine was performed according to a known procedure.[16] A solution of 1 mmol of thiirane **5** and 1 mmol (247 mg) tris(diethylamino)phosphine in dry THF (5 mL) was heated at reflux for 1.5–2 h. After evaporation of the solvent, the crude mixture was purified chromatographically (SiO_2), using a 3:2-mixture of hexane and CH_2Cl_2. Products **6** were additionally purified by crystallization from petroleum ether or hexane.

2-(1,2,2-Triphenylvinyl)thiophene (**6a**).[10] Yield: 189 mg (56%). Mp 196.4–198.5 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.58 (*dd*, $J_{H,H}$ = 3.5, 1.1 Hz, 1CH_{arom}); 6.77 (*dd*, $J_{H,H}$ = 5.2, 3.6 Hz, 1CH_{arom}); 6.98–7.00 (*m*, 2CH_{arom}); 7.04–7.07 (*m*, 3CH_{arom}); 7.12 (*dd*, $J_{H,H}$ = 5.2, 1.1 Hz, 1CH_{arom}); 7.14–7.19 (*m*, 5CH_{arom}); 7.23–7.25 (*m*, 5CH_{arom}). ^{13}C-NMR: 126.0, 126.1, 126.4, 126.9, 127.0, 127.6, 127.7, 128.2, 129.5, 130.8, 130.9, 131.3 (12 signals for 18CH_{arom}); 133.9, 141.2, 143.2, 143.6, 146.6 (4C_{arom}, 2C=). IR (KBr): 3048*m*, 3018*m*, 1595*m*, 1571*m*, 1489*s*, 1442*s*, 1430*m*, 1255*m*, 1227*m*, 1183*m*, 1073*m*, 1027*m*, 855*m*, 827*m*, 700*vs*, 648*m*, 634*m*. Anal. Calcd for $C_{24}H_{18}S$ (338.46): C 85.17, H 5.36, S 9.47. Found: C 84.93, H 5.31, S 9.37.

2-(1,2,2-Triphenylvinyl)selenophene (**6b**). Yield: 142 mg (36.8%). Mp 142 °C (dec.). ^{1}H-NMR: 6.76 (*dd*, $J_{H,H}$ = 3.8, 0.8 Hz, 1CH_{arom}); 6.96–7.00 (*m*, 3CH_{arom}); 7.04–7.07 (*m*, 3CH_{arom}); 7.15–7.17 (*m*, 3CH_{arom}); 7.20–7.22 (*m*, 2CH_{arom}); 7.28–7.31 (*m*, 5CH_{arom}); 7.84 (*dd*, $J_{H,H}$ = 5.6, 0.8 Hz, 1CH_{arom}). ^{13}C-NMR: 126.3, 126.9, 126.4, 127.4, 127.5, 127.7, 128.5, 128.6, 130.8, 131.0, 131.3, 132.1 (12 signals for 18CH_{arom}); 136.3, 140.7, 143.2, 143.3, 143.4, 152.3 (4C_{arom}, 2C=). IR (KBr): 3074*m*, 3048*m*, 3017*m*, 1597*m*, 1574*m*, 1488*s*, 1443*s*, 1225*m*, 1227*m*, 1154*m*, 1074*m*, 1027*m*, 829*m*, 815*m*, 773*vs*, 735*vs*, 646*m*,

629*m*. Anal. Calcd for $C_{24}H_{18}Se$ (385.36): C 74.80, H 4.71. Found: C 74.73, H 4.68.

2-[1-(2-Furyl)-2,2-diphenylvinyl]furan (**6c**). Yield: 231 mg (74.0%). Mp 140.1–142.3 °C (petroleum ether/CH_2Cl_2). ^{1}H-NMR: 6.07 (*dd*, $J_{H,H}$ = 3.4, 0.5 Hz, $2CH_{arom}$); 6.29 (*dd*, $J_{H,H}$ = 3.4, 1.9 Hz, $2CH_{arom}$); 7.09, 7.12 (*2d*, $J_{H,H}$ = 2.1 Hz, $4CH_{arom}$); 7.18–7.23 (*m*, $8CH_{arom}$). ^{13}C-NMR: 111.0, 112.0, 127.1, 127.8, 130.2, 141.6 (6 signals for $16CH_{arom}$); 119.7, 142.0, 143.3, 153.3 (4 signals for $4C_{arom}$, 2C=). IR (KBr): 3077*m*, 3048*m*, 3032*m*, 1596*m*, 1575*m*, 1486*s*, 1442*s*, 1379*m*, 1304*m*, 1216*s*, 1159*s*, 1135*s*, 1072*s*, 1016*vs*, 976*s*, 933*s*, 886*s*, 819*m*, 742*vs*, 700*vs*, 633*vs*, 596*vs*. Anal. Calcd for $C_{22}H_{16}O_2$ (312.36): C 84.59, H 5.16. Found: C 84.40, H 5.09.

2-[2,2-Diphenyl-1-(2-thienyl)vinyl]thiophene (**6d**).[3] Yield: 235 mg (68.3%). Mp 161.6–164 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.77 (*dd*, $J_{H,H}$ = 3.7, 1.2 Hz, $2CH_{arom}$); 6.81 (*dd*, $J_{H,H}$ = 5.2, 3.7 Hz, $2CH_{arom}$); 7.15–7.22 (*m*, $12CH_{arom}$). ^{13}C-NMR: 126.1, 126.3, 127.0, 128.0, 129.7, 130.6 (6 signals for $16CH_{arom}$); 126.6, 142.3, 143.2, 145.6 (4 signals for $4C_{arom}$, 2C=). IR (KBr): 3072*m*, 3052*m*, 3018*m*, 1594*m*, 1574*m*, 1488*s*, 1440*s*, 1421*m*, 1245*s*, 1228*s*, 1180*m*, 1153*m*, 1074*s*, 1027*s*, 999*m*, 854*s*, 832*s*, 696*vs*, 637*s*, 576*s*. Anal. Calcd for $C_{22}H_{16}S_2$ (344.49): C 76.70, H 4.68, S 18.62. Found: C 76.74, H 4.68, S 18.36.

2-[2,2-Diphenyl-1-(selenophen-2-yl)vinyl]selenophene (**6e**). Yield: 311 mg (71%). Mp 169.3–172.2 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 7.04–7.09 (*m*, $4CH_{arom}$); 7.12–7.15 (*m*, $2CH_{arom}$); 7.21–7.25 (*m*, $8CH_{arom}$); 7.92 (*d*, $J_{H,H}$ = 1.3 Hz, $1CH_{arom}$); 7.93 (*d*, $J_{H,H}$ = 1.4 Hz, $1CH_{arom}$). ^{13}C-NMR: 126.4, 127.1, 127.6, 128.1, 128.6, 130.8, 131.3, 132.1, 132.2 (9 signals for $16CH_{arom}$); 131.0, 141.0, 141.4, 143.2, 143.7, 152.0 ($4C_{arom}$, 2C=). IR (KBr): 3080*m*, 3056*m*, 3026*m*, 1598*m*, 1489*m*, 1443*s*, 1225*m*, 1179*m*, 1079*m*, 1031*m*, 1001*m*, 838*m*, 821*m*, 751*s*, 692*vs*, 651*s*, 600*m*. Anal. Calcd for $C_{22}H_{16}Se_2$ (438.28): C 60.29, H 3.68. Found: C 60.26, H 3.69.

2-[2,2-Diphenyl-1-(2-thienyl)vinyl]furan (**6f**). Yield: 252 mg (76.8%). Mp 150.1–152.4 °C (hexane). ^{1}H-NMR: 6.05 (*d*, $J_{H,H}$ = 3.2 Hz, $1CH_{arom}$); 6.28 (*dd*, $J_{H,H}$ = 3.2, 1.7 Hz, $1CH_{arom}$); 6.77 (*dd*, $J_{H,H}$ = 3.5, 0.9 Hz, $1CH_{arom}$); 6.82 (*dd*, $J_{H,H}$ = 5.0, 3.6 Hz, $1CH_{arom}$); 7.08–7.09 (*m*, $2CH_{arom}$); 7.18–7.24 (*m*, $10CH_{arom}$). ^{13}C-NMR: 111.0, 112.1, 126.2, 126.3, 126.9, 127.1, 127.8, 128.0, 129.6, 129.9, 130.8, 141.6 (12 signals for $16CH_{arom}$); 123.1, 142.3, 142.9, 143.4, 143.5, 154.8 ($4C_{arom}$, 2C=). IR (KBr): 3074*m*, 3043*m*, 3020*m*, 1597*m*, 1573*m*, 1489*s*, 1441*s*, 1425*m*, 1353*m*, 1224*s*, 1157*m*, 1112*m*, 1018*s*, 932*m*, 854*m*, 815*m*, 754*vs*, 699*vs*, 625*m*. Anal. Calcd for $C_{22}H_{16}OS$ (328.43): C 80.45, H 4.91, S 9.76. Found: C 80.23, H 4.79, S 9.66.

2-[Fluoren-9-ylidene(phenyl)methyl]thiophene (**6g**). Yield: 207 mg (61.6%). Mp 188.8–190.3 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.59 (*d*, $J_{H,H}$ = 8.0 Hz, 1CH_{arom}); 6.92 (*dt*, $J_{H,H}$ = 8.0, 1.1 Hz 1CH_{arom}); 7.04–7.07 (*m*, 2CH_{arom}); 7.13 (*dd*, $J_{H,H}$ = 5.5, 3.4 Hz, 1CH_{arom}); 7.20 (*dd*, $J_{H,H}$ = 3.4, 1.1 Hz, 1CH_{arom}); 7.24 (*dt*, $J_{H,H}$ = 7.4, 0.8 Hz, 1CH_{arom}); 7.27–7.30 (*m*, 1CH_{arom}); 7.44 (*brs*, 5CH_{arom}); 7.49 (*dd*, $J_{H,H}$ = 5.0, 1.1 Hz, 1CH_{arom}); 7.70 (*t*, $J_{H,H}$ = 8.0 Hz, 2CH_{arom}). ^{13}C-NMR: 119.2, 119.3, 124.8, 125.0, 126.5, 126.6, 127.5, 127.9, 128.0, 128.1, 128.6, 128.7, 128.8, 129.8 (14 signals for 16CH_{arom}); 136.2, 137.3, 138.5, 138.6, 140.6, 140.7, 142.8, 144.9 (6C_{arom}, 2C=). IR (KBr): 3054*m*, 3031*m*, 3019*m*, 1606*m*, 1565*m*, 1441*s*, 1339*m*, 1283*m*, 1218*m*, 1192*m*, 1155*m*, 1072*m*, 1027*m*, 985*m*, 917*m*, 866*m*, 852*m*, 779*vs*, 762*vs*, 731*vs*, 712*vs*, 697*s*, 653*m*. Anal. Calcd for $C_{24}H_{16}S$ (336.45): C 85.68 H 4.79, S 9.53. Found: C 85.64, H 4.79, S 9.56.

2-[Fluoren-9-ylidene(phenyl)methyl]selenophene (**6h)**: Yield: 249 mg (65.0%). Mp 190 °C (dec.) (hexane/CH_2Cl_2). ^{1}H-NMR: 6.58 (*d*, $J_{H,H}$ = 8.0 Hz, 1CH_{arom}); 6.94 (*t*, $J_{H,H}$ = 8.0 Hz, 1CH_{arom}); 7.08 (*t*, $J_{H,H}$ = 8.0 Hz, 1CH_{arom}); 7.25–7.29 (*m*, 2CH_{arom}); 7.31 (*dt*, $J_{H,H}$ = 7.9, 0.8 Hz 1CH_{arom}); 7.37 (*dd*, $J_{H,H}$ = 5.6, 3.6 Hz 1CH_{arom}); 7.43 (*dd*, $J_{H,H}$ = 3.6, 1.1 Hz, 1CH_{arom}); 7.47 (*brs*, 5CH_{arom}); 7.72 (*d*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}); 7.74 (*d*, $J_{H,H}$ = 7.6 Hz, 1CH_{arom}); 8.24 (*dd*, $J_{H,H}$ = 5.6, 1.1 Hz, 1CH_{arom}). ^{13}C-NMR: 119.2, 119.3, 125.1, 125.2, 126.4, 126.6, 127.8, 127.9, 128.6, 128.8, 129.6, 129.9, 130.8, 134.1 (14 signals for 16CH_{arom}); 135.3, 138.6, 138.7, 139.8, 140.6, 143.2, 151.7 (7 signals for 6C_{arom}, 2C=). IR (KBr): 3056*m*, 3030*m*, 3017*m*, 1605*m*, 1562*m*, 1441*s*, 1426*s*, 1340*m*, 1260*m*, 1178*m*, 1109*m*, 1072*m*, 944*m*, 866*m*, 777*vs*, 757*s*, 697*vs*, 672*m*. Anal. Calcd for $C_{24}H_{16}Se$ (383.34): C 75.20 H 4.21. Found: C 75.31, H 4.19.

2-[(1,2-Diphenyl-2-(2-thienyl)vinyl)thiophene (**6i**; mixture of (*E*/*Z*)-isomers).[4] Yield: 298 mg (86.1%). Mp 149.1–151.4 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.37 (*dd*, $J_{H,H}$ = 3.7, 1.1 Hz 1CH_{arom}); 6.70 (*dd*, $J_{H,H}$ = 3.7, 1.3 Hz 1CH_{arom}); 6.89 (*dd*, $J_{H,H}$ = 5.1, 3.6 Hz 1CH_{arom}); 7.05 (*dd*, $J_{H,H}$ = 5.0, 1.1 Hz 1CH_{arom}); 7.10 (*brs*, 6CH_{arom}); 7.24–7.25 (*m*, 2CH_{arom}); 7.38–7.40 (*m*, 4CH_{arom}). ^{13}C-NMR: 125.8, 126.5, 126.7, 126.8, 126.9, 127.6, 128.0, 128.8, 129.4, 129.7, 130.9, 131.0 (12 signals for 16CH_{arom}); 133.1, 134.7, 142.3, 142.7, 145.8, 145.9 (4C_{arom}, 2C=). IR (KBr): 3058*m*, 3023*m*, 2962*m*, 1596*m*, 1468*m*, 1442*s*, 1351*m*, 1261*m*, 1212*m*, 1155*m*, 1071*m*, 1056*m*, 856*m*, 852*m*, 811*s*, 744*s*, 724*s*, 695*vs*, 615*m*. Anal. Calcd for $C_{22}H_{16}S_2$ (344.49): C 76.70 H 4.68, S 18.62. Found: C 76.60, H 4.79, S 18.62.

2-[1-Phenyl-2,2-bis(2-thienyl)vinyl]thiophene (**6j**). Yield: 82 mg (23.4%). Mp 168.8–171.3 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.55 (*dd*, $J_{H,H}$ = 3.8, 1.1 Hz 1CH_{arom}); 6.56 (*dd*, $J_{H,H}$ = 3.7, 1.1 Hz 1CH_{arom}); 6.74 (*dd*, $J_{H,H}$ = 5.0, 3.7 Hz 1CH_{arom}); 6.79 (*dd*, $J_{H,H}$ = 5.0, 3.7 Hz 1CH_{arom}); 7.04–7.07 (*m*, 2CH_{arom}); 7.09 (*dd*, $J_{H,H}$ = 5.1, 1.1 Hz 1CH_{arom}); 7.19 (*dd*, $J_{H,H}$ = 5.1, 1.1 Hz 1CH_{arom}); 7.32–7.37 (*m*, 5CH_{arom}); 7.42 (*dd*,

$J_{H,H}$ = 3.7, 2.6 Hz 1CH_{arom}). ^{13}C-NMR: 125.9, 126.0, 126.8, 127.1, 127.3, 127.5, 128.0, 128.6, 129.6, 129.8, 130.0, 130.8 (12 signals for 14CH_{arom}); 125.6, 135.6, 142.0, 142.7, 145.5, 145.6 (4C_{arom}, 2C=). IR (KBr): 3098*m*, 3060*m*, 1485*m*, 1440*s*, 1426*s*, 1351*m*, 1235*m*, 1204*m*, 1173*m*, 1096*m*, 1059*m*, 1024*s*, 849*s*, 852*m*, 729*s*, 695*vs*, 596*m*. ESI-MS: 352 (51, $[M+2]^+$), 351 (100, $[M+1]^+$), 350 (84, M^+). HR-ESI-MS (MeOH + NaI): 351.03304 (calcd 351.03301 for $C_{20}H_{15}S_3$, $[M+1]^+$).

2-[2,2-Di(selenophen-2-yl)-1-(2-thienyl)vinyl]thiophene (**6l**). Yield: 168 mg (37.6%). Mp 207.8–209.6 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.92 (*d*, $J_{H,H}$ = 1.3 Hz, 1CH_{arom}); 6.93 (*d*, $J_{H,H}$ = 1.1 Hz, 1CH_{arom}); 6.97 (*d*, $J_{H,H}$ = 3.7 Hz, 1CH_{arom}); 6.98 (*d*, $J_{H,H}$ = 3.7 Hz, 1CH_{arom}), 7.15 (*d*, $J_{H,H}$ = 1.1 Hz, 1CH_{arom}); 7.16 (*d*, $J_{H,H}$ = 1.1 Hz, 1CH_{arom}); 7.19 (*d*, $J_{H,H}$ = 3.8 Hz, 1CH_{arom}); 7.20 (*d*, $J_{H,H}$ = 3.8 Hz, 1CH_{arom}); 7.36 (*dd*, $J_{H,H}$ = 5.2, 1.3 Hz, 2CH_{arom}); 8.06 (*dd*, $J_{H,H}$ = 5.6, 1.2 Hz, 2CH_{arom}). ^{13}C-NMR: 126.7, 128.0, 129.0, 130.4, 132.5, 133.6 (6 signals for 12CH_{arom}); 126.7, 131.1, 144.0, 150.1 (4C_{arom}, 2C=). IR (KBr): 3091*m*, 3070*m*, 1450*m*, 1431*s*, 1344*m*, 1234*s*, 1189*m*, 1124*m*, 1070*m*, 1046*s*, 1008*m*, 846*s*, 799*m*, 760*s*, 709*vs*, 695*vs*, 640*m*, 589*m*. Anal. Calcd for $C_{18}H_{12}S_2Se_2$ (450.34): C 48.01, H 2.69, S 14.24. Found: C 48.07, H 2.76, S 14.45.

2-[1,2,2-Tris(2-thienyl)vinyl]furan (**6m**). Yield: 250 mg (73.5%). Mp 155.2–157.0 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.16 (*dd*, $J_{H,H}$ = 3.3, 0.6 Hz 1CH_{arom}); 6.39 (*dd*, $J_{H,H}$ = 3.3, 1.7 Hz 1CH_{arom}); 6.85 (*dd*, $J_{H,H}$ = 3.7, 1.1 Hz 1CH_{arom}); 6.90–6.95 (*m*, 6CH_{arom}); 7.28–7.31 (*m*, 2CH_{arom}); 7.33 (*dd*, $J_{H,H}$ = 1.7, 0.6 Hz 1CH_{arom}). ^{13}C-NMR: 111.5, 112.5, 126.5, 126.6, 126.8, 127.4, 127.6, 127.8, 128.9, 129.9, 130.1, 142.2, (12CH_{arom}); 123.8, 129.5, 142.6, 144.3, 145.0, 153.7 (4C_{arom}, 2C=). IR (KBr): IR (KBr): 3095*m*, 3080*m*, 1472*m*, 1432*s*, 1349*m*, 1245*m*, 1202*m*, 1159*m*, 1074*m*, 1059*m*, 1021*m*, 935*m*, 855*s*, 814*m*, 750*s*, 701*vs*, 596*m*. Anal. Calcd for $C_{18}H_{12}OS_3$ (340.48): C 63.50 H 3.55, S 28.25. Found: C 63.57, H 3.61, S 28.61.

2-[1-Phenyl-2,2-di(selenophen-2-yl)vinyl]thiophene (**6n**). Yield: 306 mg (68.9%). Mp 188.2–190.4 °C (hexane/CH_2Cl_2). ^{1}H-NMR: 6.55 (*d*, $J_{H,H}$ = 3.7 Hz, 1CH_{arom}); 6.79–6.80 (*m,* 1CH_{arom}); 6.89 (*d*, $J_{H,H}$ = 3.8 Hz, 1CH_{arom}); 6.99 (*dd*, $J_{H,H}$ = 5.5, 3.8 Hz, 1CH_{arom}); 7.20 (*d*, $J_{H,H}$ = 5.1 Hz, 1CH_{arom}); 7.25 (*d*, $J_{H,H}$ = 5.3 Hz, 1CH_{arom}); 7.29 (*dd*, $J_{H,H}$ = 5.5, 3.7 Hz, 1CH_{arom}); 7.34–7.42 (*m*, 5CH_{arom}); 7.82 (*d*, $J_{H,H}$ = 5.6 Hz, 1CH_{arom}); 8.17 (*d*, $J_{H,H}$ = 5.6 Hz, 1CH_{arom}). ^{13}C-NMR: 125.9, 127.9, 128.3, 128.4, 129.0, 129.5, 130.4, 131.1, 132.2, 132.4, 132.9, 133.4 (12 signals for 14CH_{arom}); 129.9, 134.6, 141.7, 145.5, 150.2, 150.9 (4C_{arom}, 2C=). IR (KBr): 3094*m*, 3058*m*, 1483*m*, 1439*s*, 1345*m*, 1236*s*, 1199*m*, 1155*m*, 1061*m*, 1017*m*, 998*m*, 836*m*, 783*m*, 725*s*, 689*vs*, 639*m*, 614*m*. Anal. Calcd for $C_{20}H_{14}SSe_2$ (444.31): C 54.06 H 3.18, S 7.22. Found: C 54.05, H 3.26, S 7.46.

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