Synthesis of 5-(Arylselanyl)-2-(arylsulfanyl)benzoates by [3 + 3] Cyclocondensation of 3-(Arylsulfanyl)-1-(silyloxy)buta-1,3-dienes with 2-(Arylselanyl)-3-(silyloxy)alk-2-en-1-ones

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Functionalized 5-(arylselanyl)-2-(arylsulfanyl)benzoates were prepared by [3 + 3] cyclocondensation of 3-(arylsulfanyl)-1-(silyloxy)buta-1,3-dienes with 2-(arylselanyl)-3-(silyloxy)-alk-2-en-1-ones.

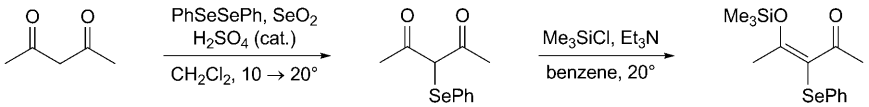
Introduction. – Diaryl selenides possess interesting biological properties such as antimicrobial, antitumor, and antioxidant activities. In addition, they have been used in the field of material sciences (*e.g.*, as conductive and supraconductive organic molecules) [1]. Due to the unstable nature of organoselenium compounds, their synthesis is considerably more difficult than the synthesis of the corresponding S analogs. In fact, most of the methods developed for the synthesis of organosulfur compounds cannot be easily adapted to the synthesis of organoselenium derivatives. Aliphatic organoselenium compounds have been prepared by reaction of selenolates with various electrophiles (*e.g.*, organic halides, acyl chlorides, epoxides, and enones) [2]. Diaryl selenides are, in general, more difficult to prepare than aliphatic selenides, because nucleophilic substitution reactions cannot be applied. Unsymmetrical diaryl selenides are more difficult to prepare than symmetrical ones. Diaryl selenides have been prepared by reaction of selenolates with aryl halides [3] and by reaction of organometallic reagents (*e.g.*, organolithium compounds, *Grignard* reagents, or cuprates) with diaryl diselenides or arylselenyl bromides [4]. Despite their great utility, there are several drawbacks such as low regioselectivity, harsh reaction conditions (high temperature), reduction, and formation of diselenides. An additional problem lies in the synthesis of the required starting materials, as highly functionalized or sterically encumbered halogenated arenes are not readily available, and their synthesis can be a very difficult and tedious task. As a result, highly substituted or functionalized diaryl selenides are not readily available by the methods known to date for the formation of C–Se bonds.

To address these problems associated with the synthesis of diaryl selenides, we have envisaged the application of a building-block strategy which relies on the use of appropriate Se-containing molecules in cyclization reactions. Applications of this approach to the synthesis of carbacyclic molecules have only scarcely been reported so far. Six-membered rings were prepared by [4 + 2] cycloaddition of 2-(phenylselanyl)-

buta-1,3-dienes with alkenes and alkynes [5]. Recently, we have reported [6] the synthesis of 5-(phenylselanyl)salicylates by formal [3 + 3] cyclizations [7] of 1,3-bis(silyloxy)buta-1,3-dienes [8] with 2-(arylselanyl)-3-(silyloxy)alk-2-en-1-ones. Here, we report, for the first time, the cyclization of 2-(arylselanyl)-3-(silyloxy)-2-en-1-ones with 3-(arylsulfanyl)-1-(silyloxy)buta-1,3-dienes. These transformations allow a convenient synthesis of novel 5-(arylselenyl)-2-(arylsulfanyl)benzoates which can be regarded as mixed diaryl sulfides and diaryl selenides. The synthesis of this type of highly substituted and functionalized products has not been previously reported. It can be anticipated that the products are not readily available by other methods.

Results and Discussion. – The reaction of acetylacetone (**1**) with SeO_2 and diphenyl diselenide, in the presence of catalytic amounts of H_2SO_4, afforded the 2-(phenylselanyl)-1,3-dione **2** (*Scheme 1*) [9]. The silylation of **2** with Me_3SiCl afforded the novel 3-(silyloxy)-2-en-1-one **3**. The known 3-(arylsulfanyl)-1-(trimethylsilyloxy)buta-1,3-dienes **4a**–**4k** were prepared from methyl acetoacetate, methyl 3-oxopentanoate, and various thiophenols in two steps [10].

Scheme 1. *Synthesis of* **3**



1 **2** (52%) **3** (90%)

The $TiCl_4$-mediated cyclization of **3** with dienes **4a**–**4k** afforded the novel 2-(arylsulfanyl)-5-(phenylselanyl)benzoates **5a**–**5k** in 43–67% yield (*Scheme 2* and *Table*). Products **5a**–**5k** contain a diaryl sulfide and a diaryl selenide moiety. The yields of products **5d** and **5j**, derived from dienes containing no terminal substituent, were higher than the yields of products **5f** and **5k**, respectively. The yields of the products derived from dienes **4b** and **4c**, containing an electron-withdrawing Cl-atom attached to

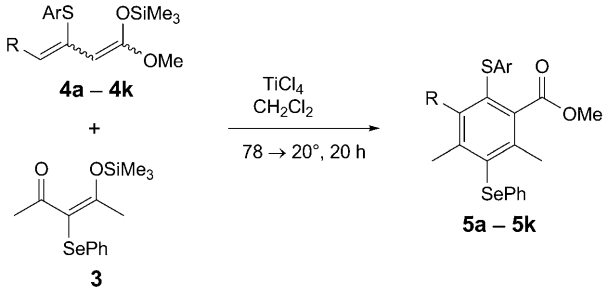
Table. *Synthesis of* **5a**–**5k**

4 and **5**	R	Ar	Yield of **5** [%][a])
a	H	Ph	67
b	Me	4-Cl–C_6H_4	43
c	H	3-Cl–C_6H_4	51
d	H	4-Me–C_6H_4	61
e	H	3-Me–C_6H_4	60
f	Me	4-Me–C_6H_4	47
g	H	3-MeO–C_6H_4	63
h	H	4-MeO–C_6H_4	64
i	H	Naphthalen-2-yl	45
j	H	4-Et–C_6H_4	59
k	Me	4-Et–C_6H_4	47

[a]) Yields of isolated products.

the aryl group, were lower than the yields of those products which are derived from dienes containing more electron-rich aryl groups. This can be explained by the decreased nucleophilicity of dienes **4b** and **4c**. The yield of product **5i** is relatively low, which might be explained by steric hindrance of the naphthyl group.

Scheme 2. *Synthesis of* **5a**–**5k**



In conclusion, we have reported the first synthesis of 5-(arylselanyl)-2-(arylsulfanyl)benzoates, mixed diaryl sulfides and selenides, by [3 + 3] cyclocondensation of 3-(arylsulfanyl)-1-(silyloxy)buta-1,3-dienes with 2-(arylselanyl)-3-(silyloxy)alk-2-en-1-ones.

Experimental Part

General. All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. M.p.: Microheating table *HMK 67/1825 Kuestner* (*Büchi* apparatus); uncorrected. Column chromatography (CC): silica gel *60* (SiO_2; 0.063–0.200 mm, 70–230 mesh). IR Spectra: *Nicolet 380* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AVANCE 300 II* and *Bruker AVANCE 250 II* spectrometer in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS and HR-EI-MS: *Finnigan MAT 95-XP* mass spectrometer at 70 eV; in *m*/*z*.

4-(Phenylselanyl)heptane-3,5-dione. To a CH_2Cl_2 suspension (35 ml) of SeO_2 (1.11 g, 10.0 mmol), diphenyl diselenide (6.24 g, 20.0 mmol) and a cat. amount of conc. H_2SO_4 (0.1 ml, 2.0 mmol) was added heptane-3,5-dione (2.3 ml, 17.0 mmol), at 10°. The mixture was stirred for 14 h at 20°. The mixture was poured into CH_2Cl_2 (100 ml), and the aq. and the org. layer were separated. The latter was washed with a sat. aq. soln. of $NaHCO_3$ (20 ml), dried (Na_2SO_4), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by CC (SiO_2; AcOEt, heptanes) to give the title compound (1.33 g, 47%). Yellowish oil. IR (neat): 3069*w*, 2976*w*, 2937*w*, 2877*w*, 1695*m*, 1575*m*, 1557*m*, 1475*m*, 1458*m*, 1436*m*, 1401*m*, 1375*m*, 1337*m*, 1296*m*, 1240*m*, 1187*m*, 1156*m*, 1099*m*, 1064*m*, 1019*m*, 997*m*, 886*w*, 847*m*, 805*m*, 731*s*, 688*s*, 666*m*, 614*w*. ^1H-NMR (300 MHz): 1.02 (*t*, ^3J = 7.4, 2 Me); 2.71 (*q*, ^3J = 7.6, 2 CH_2); 3.61 (*s*, CH); 7.07–7.12 (*m*, 2 arom. H); 7.13–7.20 (*m*, 3 arom. H). ^{13}C-NMR (75 MHz): 13.7, 13.9 (Me); 31.2, 31.3 (CH_2); 61.4 (CH); 125.0 (arom. CH); 126.6, 128.3 (2 arom. CH); 130.5 (arom. C); 197.0, 200.0 (C=O). GC/MS: 284 (43, M^+), 282 (10), 280 (22), 255 (14), 254 (11), 253 (13), 230 (23), 228 (21), 226 (14), 225 (13), 224 (14), 172 (11). HR-EI-MS: 284.03100 (M^+, $C_{13}H_{16}O_2Se^+$; calc. 284.03155).

General Procedure for the Synthesis of the Benzoates **5a**–**5k**. To a CH_2Cl_2 soln. (6 ml/mmol of **3**) of **4a**–**4k** (1.5 mmol) and of **3** (1.5 mmol) was added $TiCl_4$ (2.25 mmol) at −78°. The soln. was allowed to warm to 20° within 20 h. To the soln. was added NH_4Cl (20 ml). The org. and the aq. layer were separated, and the latter was extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layers were dried ($MgSO_4$), filtered, and the filtrate was concentrated *in vacuo*, and the residue was purified by CC (SiO_2; AcOEt/heptane 1:9): **5a**–**5k**, all as highly viscous oils.

Methyl 2,4-Dimethyl-3-(phenylselanyl)-6-(phenylsulfanyl)benzoate (**5a**). Yield: 429 mg (67%). IR (KBr): 3056*w*, 2992*w*, 2949*w*, 2922*w*, 2850*w*, 2664*w*, 1083*m*, 1738*m*, 1710*s*, 1650*m*, 1571*m*, 1473*m*, 1438*s*, 1303*m*, 1247*m*, 1195*s*, 1153*s*, 1099*s*, 1067*m*, 1022*s*, 1000*m*, 886*m*, 844*m*, 803*m*, 745*s*, 703*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.32 (*s*, Me); 2.34 (*s*, Me); 3.54 (*s*, MeO); 7.13–7.30 (*m*, 11 arom. H). ^{13}C-NMR (63 MHz): 18.9 (Me); 25.1 (Me); 49.8 (MeO); 110.2, 125.0 (arom. CH); 126.3 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.3, 128.6, 128.9, 129.0, 129.7 (arom. CH); 130.2, 130.4, 131.2 (arom. C); 132.4, 133.4, 134.0 (arom. CH); 157.9, 164.5 (arom. C); 196.7 (C). EI-MS: 428 (18), 427 (100, $[M-H]^+$), 411 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 427.09715 ($[M-H]^+$, $C_{22}H_{19}O_2SSe^+$; calc. 427.02710).

Methyl 2-[(4-Chlorophenyl)sulfanyl]-3,4,6-trimethyl-5-(phenylselanyl)benzoate (**5b**). Yield: 306 mg (43%). IR (KBr): 3055*w*, 2991*w*, 2948*w*, 2923*w*, 2850*w*, 2664*w*, 1082*m*, 1738*m*, 1710*s*, 1650*m*, 1572*m*, 1473*m*, 1437*s*, 1303*m*, 1247*m*, 1195*s*, 1153*s*, 1098*s*, 1067*m*, 1022*s*, 1000*m*, 886*m*, 844*m*, 803*m*, 745*s*, 703*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.12 (*s*, Me); 2.23 (*s*, Me); 2.34 (*s*, Me); 3.75 (*s*, MeO); 7.13–7.50 (*m*, 9 arom. H). ^{13}C-NMR (63 MHz): 18.9 (Me); 20.1 (Me); 25.1 (Me); 51.0 (MeO); 110.2, 123.8, 124.1, 124.3 (arom. CH); 126.3 (arom. C); 127.4 (2 arom. CH); 127.9, 128.0, 128.2 (arom. CH); 128.5, 130.1, 130.5, 130.9, 131.0, 132.3, 138.6, 144.3 (arom. C); 167.1 (C). EI-MS: 477 (39), 475 (100, $[M-H]^+$), 411 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 475.03207 ($[M-H]^+$, $C_{23}H_{20}ClO_2SSe^+$; calc. 475.00378).

Methyl 6-[(3-Chlorophenyl)sulfanyl]-2,4-dimethyl-3-(phenylselanyl)benzoate (**5c**). Yield: 253 mg (51%). IR (KBr): 3056*w*, 2992*w*, 2948*w*, 2921*w*, 2850*w*, 2666*w*, 1083*m*, 1739*m*, 1710*s*, 1571*m*, 1473*m*, 1438*s*, 1303*m*, 1248*m*, 1195*s*, 1153*s*, 1099*s*, 1067*m*, 1022*s*, 1000*m*, 887*m*, 845*m*, 803*m*, 746*s*, 703*s*, 689*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.32 (*s*, Me); 2.34 (*s*, Me); 3.56 (*s*, MeO); 7.10–7.80 (*m*, 10 arom. H). ^{13}C-NMR (63 MHz): 20.1 (Me); 21.1 (Me); 51.1 (MeO); 110.2 (arom. CH); 126.3 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.3, 128.6, 128.9, 129.0, 129.7 (arom. CH); 130.2, 130.4, 131.2 (arom. C); 132.4, 133.4, 134.0 (arom. CH); 157.9, 160.2, 164.5 (arom. C); 170.7 (C). EI-MS: 463 (38), 461 (100, $[M-H]^+$), 411 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 461.03207 ($[M-H]^+$, $C_{22}H_{18}ClO_2SSe^+$; calc. 460.98813).

Methyl 2,4-Dimethyl-6-[(4-methylphenyl)sulfanyl]-3-(phenylselanyl)benzoate (**5d**). Yield: 403 mg (61%). IR (KBr): 3056*w*, 2992*w*, 2948*w*, 2921*w*, 2850*w*, 2665*w*, 1083*m*, 1738*m*, 1710*s*, 1571*m*, 1473*m*, 1438*s*, 1303*m*, 1248*m*, 1195*s*, 1153*s*, 1099*s*, 1067*m*, 1022*s*, 1000*m*, 886*m*, 844*m*, 803*m*, 745*s*, 703*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.0 (*s*, Me); 2.32 (*s*, Me); 2.34 (*s*, Me); 3.49 (*s*, MeO); 7.10–7.42 (*m*, 10 arom. H). ^{13}C-NMR (63 MHz): 18.9 (Me); 20.1 (Me); 21.1 (Me); 51.1 (MeO); 110.2 (arom. CH); 126.3 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.3, 128.6, 128.8, 129.0, 129.4 (arom. CH); 130.2, 130.4, 131.1 (arom. C); 132.6, 133.5, 134.0 (arom. CH); 157.9, 160.2, 164.5 (arom. C); 170.7 (C). EI-MS: 442 (18), 441 (100, $[M-H]^+$), 414 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 441.09715 ($[M-H]^+$, $C_{23}H_{21}O_2SSe^+$; calc. 441.04275).

Methyl 2,4-Dimethyl-6-[(3-methylphenyl)sulfanyl]-3-(phenylselanyl)benzoate (**5e**). Yield: 403 mg (61%). IR (KBr): 3055*w*, 2992*w*, 2948*w*, 2931*w*, 2850*w*, 2665*w*, 1083*m*, 1738*m*, 1710*s*, 1571*m*, 1473*m*, 1438*s*, 1303*m*, 1195*s*, 1154*s*, 1099*s*, 1067*m*, 1021*s*, 1000*m*, 885*m*, 843*m*, 803*m*, 745*s*, 704*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.10 (*s*, Me); 2.31 (*s*, Me); 2.33 (*s*, Me); 3.49 (*s*, MeO); 7.10–7.40 (*m*, 10 arom. H). ^{13}C-NMR (63 MHz): 18.8 (Me); 20.1 (Me); 21.1 (Me); 51.1 (MeO); 110.2 (arom. CH); 126.3 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.3, 128.6, 128.8, 129.0, 129.4 (arom. CH); 130.2, 130.4, 131.1 (arom. C); 132.6, 133.5, 134.0 (arom. CH); 157.9, 160.2, 164.5 (arom. C); 170.7 (C). EI-MS: 442 (18), 441 (100, $[M-H]^+$), 414 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 441.09716 ($[M-H]^+$, $C_{23}H_{21}O_2SSe^+$; calc. 441.04275).

Methyl 2,4,5-Trimethyl-6-[(4-methylphenyl)sulfanyl]-3-(phenylselanyl)benzoate (**5f**). Yield: 331 mg (47%). IR (KBr): 3056*w*, 2992*w*, 2949*w*, 2931*w*, 2850*w*, 2666*w*, 1083*m*, 1738*m*, 1710*s*, 1571*m*, 1473*m*, 1438*s*, 1303*m*, 1196*s*, 1153*s*, 1099*s*, 1067*m*, 1023*s*, 1000*m*, 885*m*, 844*m*, 804*m*, 745*s*, 703*s*, 687*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.12 (*s*, Me); 2.23 (*s*, Me); 2.31 (*s*, Me); 2.33 (*s*, Me); 3.50 (*s*, MeO); 7.10–7.48 (*m*, 9 arom. H). ^{13}C-NMR (63 MHz): 18.8 (Me); 20.0 (Me); 20.1 (Me); 21.1 (Me); 51.1 (MeO); 110.2 (arom. CH); 126.3, 126.9 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.3, 128.8, 129.0, 129.4 (arom. CH); 130.2, 130.4, 131.1 (arom. C); 132.6, 133.5, 134.0 (arom. CH); 157.9, 160.2, 164.5 (arom. C); 170.7 (C). EI-MS: 456

(18), 455 (100, $[M-H]^+$), 410 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 455.09716 ($[M-H]^+$, $C_{24}H_{23}O_2SSe^+$; calc. 455.05840).

Methyl 6-[(3-Methoxyphenyl)sulfanyl]-2,4-dimethyl-3-(phenylselanyl)benzoate (**5g**). Yield: 432 mg (63%). IR (KBr): 3056*w*, 2992*w*, 2948*w*, 2931*w*, 2850*w*, 2665*w*, 1083*m*, 1737*m*, 1710*s*, 1571*m*, 1472*m*, 1438*s*, 1303*m*, 1194*s*, 1153*s*, 1099*s*, 1068*m*, 1022*s*, 1000*m*, 885*m*, 844*m*, 804*m*, 745*s*, 703*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.13 (*s*, Me); 2.31 (*s*, Me); 3.49 (*s*, MeO); 3.51 (*s*, MeO); 7.24–7.55 (*m*, 10 arom. H). ^{13}C-NMR (63 MHz): 20.8 (Me); 21.1 (Me); 50.4 (MeO); 51.1 (MeO); 110.2 (arom. CH); 126.3 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.3, 128.6, 128.8, 129.0, 129.4 (arom. CH); 130.2, 130.4, 131.1 (arom. C); 132.6, 133.5, 134.0 (arom. CH); 157.9, 160.2, 164.5 (arom. C); 170.7 (C). EI-MS: 458 (11), 457 (100, $[M-H]^+$), 414 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 457.09716 ($[M-H]^+$, $C_{23}H_{21}O_3SSe^+$; calc. 457.03766).

Methyl 6-[(4-Methoxyphenyl)sulfanyl]-2,4-dimethyl-3-(phenylselanyl)benzoate (**5h**). Yield: 439 mg (64%). IR (KBr): 3056*w*, 2992*w*, 2948*w*, 2931*w*, 2851*w*, 2665*w*, 1083*m*, 1739*m*, 1710*s*, 1571*m*, 1473*m*, 1438*s*, 1303*m*, 1195*s*, 1153*s*, 1099*s*, 1068*m*, 1022*s*, 1000*m*, 885*m*, 845*m*, 803*m*, 745*s*, 703*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.13 (*s*, Me); 2.32 (*s*, Me); 3.50 (*s*, MeO); 3.52 (*s*, MeO); 7.24–7.55 (*m*, 10 arom. H). ^{13}C-NMR (63 MHz): 20.8 (Me); 21.1 (Me); 50.4 (MeO); 51.1 (MeO); 110.2 (arom. CH); 126.3 (arom. C); 127.5 (arom. CH); 127.9 (arom. C); 128.4, 128.6, 128.8, 129.0, 129.4 (arom. CH); 130.2, 130.4, 131.1 (arom. C); 132.6, 133.5, 134.0 (arom. CH); 157.9, 160.2, 164.5 (arom. C); 170.7 (C). EI-MS: 458 (11), 457 (100, $[M-H]^+$), 414 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (17). HR-EI-MS: 457.09716 ($[M-H]^+$, $C_{23}H_{21}O_3SSe^+$; calc. 457.03766).

Methyl 2,4-Dimethyl-6-[(naphthalen-2-yl)sulfanyl]-3-(phenylselanyl)benzoate (**5i**). Yield: 322 mg (45%). IR (KBr): 3056*w*, 2992*w*, 2948*w*, 2931*w*, 2851*w*, 2665*w*, 1083*m*, 1738*m*, 1712*s*, 1571*m*, 1473*m*, 1437*s*, 1303*m*, 1270*m*, 1195*s*, 1153*s*, 1099*s*, 1067*m*, 1021*s*, 1000*m*, 885*m*, 846*m*, 803*m*, 745*s*, 704*s*, 688*s*, 608*m*. ^{1}H-NMR (250 MHz): 2.25 (*s*, Me); 2.43 (*s*, Me); 3.80 (*s*, MeO); 6.98–7.84 (*m*, 13 arom. H). ^{13}C-NMR (63 MHz): 20.8 (Me); 23.7 (Me); 51.3 (MeO); 124.9, 125.4, 125.6, 126.5, 126.7 (arom. CH); 126.9 (arom. C); 127.9 (2 arom. CH); 128.0, 128.1 (arom. CH); 128.3 (2 arom. CH); 129.7 (arom. C); 129.8, 130.0 (arom. CH); 130.7, 131.2, 131.5, 132.6, 133.6, 139.9, 144.8 (arom. C); 167.9 (C). EI-MS: 478 (11), 477 (100, $[M-H]^+$), 414 (12), 271 (61), 270 (21), 269 (86), 256 (18), 255 (49), 228 (17), 227 (13), 185 (10), 184 (16). HR-EI-MS: 477.09715 ($[M-H]^+$, $C_{26}H_{21}O_2SSe^+$; calc. 477.04275).

Methyl 6-[(4-Ethylphenyl)sulfanyl]-2,4-dimethyl-3-(phenylselanyl)benzoate (**5j**). Yield: 403 mg (59%). IR (neat): 3016*w*, 2963*w*, 2948*w*, 2928*w*, 2871*w*, 1729*s*, 1596*m*, 1491*m*, 1433*m*, 1404*w*, 1383*w*, 1285*s*, 1242*m*, 1223*m*, 1187*m*, 1142*s*, 1119*m*, 1087*m*, 1052*m*, 1014*m*, 1004*m*, 821*s*, 789*m*, 751*w*, 721*m*. ^{1}H-NMR (250 MHz): 1.09 (*t*, $J=7.2$, Me); 2.16 (*s*, Me); 2.18 (*s*, Me); 2.47 (*q*, $J=7.2$, CH_2); 3.74 (*s*, MeO); 6.93–7.17 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz): 15.4 (Me); 16.9 (Me); 28.3 (CH_2); 52.0 (MeO); 127.6 (2 arom. CH); 128.4 (2 arom. CH); 128.5, 131.9 (arom. C); 132.8, 133.0, 133.4, 133.7, 134.0, 134.9 (arom. CH); 134.1, 138.7, 139.0, 139.2, 139.8, 141.6 (arom. C); 169.7 (C). GC/EI-MS: 456 (18), 455 (100, $[M-H]^+$), 284 (5), 283 (26), 182 (10), 281 (27), 267 (7), 254 (20), 253 (97), 239 (7), 225 (15), 178 (5), 134 (4), 121 (19). HR-EI-MS: 455.13346 ($[M-H]^+$, $C_{24}H_{23}O_2SSe^+$; calc. 455.05840).

Methyl 2-[(4-Ethylphenyl)sulfanyl]-3,4,6-trimethyl-5-(phenylselanyl)benzoate (**5k**). Yield: 331 mg (47%). IR (neat): 3016*w*, 2963*w*, 2948*w*, 2928*w*, 2871*w*, 1729*s*, 1596*m*, 1491*m*, 1433*m*, 1404*w*, 1383*w*, 1285*s*, 1242*m*, 1223*m*, 1187*m*, 1142*s*, 1118*m*, 1087*m*, 1052*m*, 1014*m*, 1004*m*, 821*s*, 789*m*, 751*w*, 721*m*. ^{1}H-NMR (250 MHz): 1.09 (*t*, $J=7.2$, Me); 2.16 (*s*, Me); 2.18 (*s*, Me); 2.19 (*s*, Me); 2.48 (*q*, $J=7.2$, CH_2); 3.76 (*s*, MeO); 6.93–7.42 (*m*, 9 arom. H). ^{13}C-NMR (75 MHz): 15.4 (Me); 16.9 (Me); 18.1 (Me); 28.3 (CH_2); 52.0 (MeO); 127.6 (2 arom. CH); 128.4 (2 arom. CH); 128.5, 131.9 (arom. C); 132.8, 133.0, 133.4, 134.0, 134.9 (arom. CH); 134.1, 138.7, 139.0, 139.2, 139.8, 141.6, 141.9 (arom. C); 169.7 (C). GC/EI-MS: 470 (18), 469 (100, $[M-H]^+$), 284 (5), 283 (26), 182 (10), 281 (27), 267 (7), 254 (20), 253 (97), 239 (7), 225 (15), 178 (5), 134 (4), 121 (19). HR-EI-MS: 469.13346 ($[M-H]^+$, $C_{25}H_{25}O_2SSe^+$; calc. 469.07405).

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