DOI: 10.1002/ejoc.200600517

Intramolecular Nonbonding Interactions between Selenium and Sulfur – Spectroscopic Evidence and Importance in Asymmetric Synthesis

Marcello Tiecco,*[a] Lorenzo Testaferri,[a] Claudio Santi,[a] Cristina Tomassini,[a] Stefano Santoro,[a] Francesca Marini,[a] Luana Bagnoli,[a] Andrea Temperini,[a] and Ferdinando Costantino[b]

Keywords: Asymmetric electrophilic additions / Chiral selenenylating reagents / Noncovalent interactions / Selenium / Sulfur

Chiral sulfur-containing electrophilic selenium reagents can be employed to effect efficient asymmetric syntheses. Spectroscopic and chemical evidence demonstrate that the observed high selectivity of the asymmetric reactions is associated with a nonbonding selenium–sulfur interaction that is present in both the crystalline form and in solution.

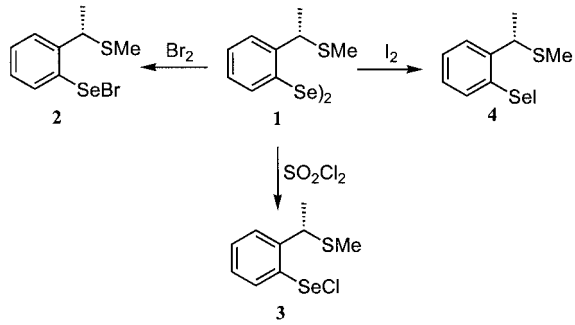
Introduction

Weak interactions play a crucial role in chemistry and biochemistry and are often responsible for several important properties of organic molecules.[1–3] Special attention has been recently devoted to the intramolecular and intermolecular attractive interactions that exist between di- and tetracoordinate sulfur, selenium, and tellurium atoms from one side, and oxygen and nitrogen atoms from the other side.[4–6] It has been observed that divalent selenium can interact with a nearby heteroatom (O, N, etc.) to form a pseudo high-valent selenium species.[4,7] Recent studies on intramolecular stabilized organoselenium compounds showed that Se–N and Se–O interactions play an important role not only in the catalytic antioxidant activity of these compounds but also in their use as reagents in synthetic organic chemistry.[8]

In recent years, chiral nonracemic electrophilic selenenylating reagents have been extensively employed by us as well as by other research groups for their efficiency in the promotion of asymmetric additions to alkenes and also for their use in cyclofunctionalization reactions.[9] A common characteristic of all these reagents is the close proximity of the selenium atom to an oxygen or nitrogen heteroatom that is linked to a chiral carbon atom. From the results of experimental and theoretical investigations, Wirth and coworkers demonstrated that in these cases a nonbonding interaction between the selenium and the heteroatom takes place.[10] Detailed investigations on the nonbonding interactions of divalent organic selenium with heteroatoms were also performed by Tomoda and coworkers.[11] It was suggested by them that these interactions will force the chiral center to move closer to the reaction center, and that this will produce a better transfer of the chiral information during the selenenylation reaction.

Recently, we have reported the synthesis of a new class of enantiopure sulfur-containing diselenides and their use as precursors to electrophilic reagents that are able to asymmetrically add to olefins.[12] All of the reactions investigated showed a very high facial selectivity that was higher than those obtained with the corresponding nitrogen- or oxygen-containing selenenylating reagents. It was suggested that these excellent results were due to the fact that the selenium–sulfur interaction is more efficient than the interactions between selenium–oxygen or –nitrogen.

In order to have unambiguous experimental evidence for the existence of this Se–S interaction, we have now carried out X-ray analysis of selenenylating reagents **2** and **3**, which are shown in Scheme 1. The NMR properties of reagents **2**–**4** and their efficiency in promoting asymmetric syntheses have also been investigated (Scheme 1).



Scheme 1. Synthesis of arylselenenyl halides.

[a] Dipartimento di Chimica e Tecnologia del Farmaco, Sezione di Chimica Organica, Università di Perugia, 06123 Perugia, Italy
[b] Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

Results and Discussion

Selenenyl derivatives **2**–**4** were obtained from the reaction of diselenide **1**[13] with the reagents indicated in Scheme 1 in diethyl ether. All compounds were obtained in almost quantitative yields, and derivatives **2** and **3** were crystallized from diethyl ether as red and yellow solids, respectively. They are stable at room temperature for several days, and compound **3** can even be purified by chromatography on a silica gel column with dichloromethane as the eluent. Iodide **4** was obtained as an oil. With respect to other selenenyl iodides, most of which are rapidly oxidized to the corresponding diselenides, compound **4** can be safely stored in the refrigerator for several days. It can be suggested that this stability is due to the formation of a five-membered chelate which arises from the Se–S interaction.

From compounds **2** and **3** crystals suitable for X-ray analysis were obtained. The ORTEP views of compounds **2** and **3** are shown in Figures 1[14] and 2,[15] respectively. Selected bond lengths and bond angles are listed in Tables 1 and 2. Compounds **2** and **3** are isostructural; the coordination geometry around the selenium atom is T-shaped with a bond angle of 178.86(5)° for **2** and 177.74(4)° for **3**. The distance between Se1 and S1 [2.497(7) Å for **2** and 2.344(2) Å for **3**] is significantly shorter than the sum of the van der Waals radii (3.7 Å),[16] and this demonstrates that an intramolecular interaction between selenium and sulfur exists. The shorter distance observed in compound **3** compared with that of compound **2** seems to indicate a stronger interaction when the counterion is chlorine, and this observation is consistent with the calculated covalency factor χ for bromide (0.826) and chloride (0.902) derivatives.[17]

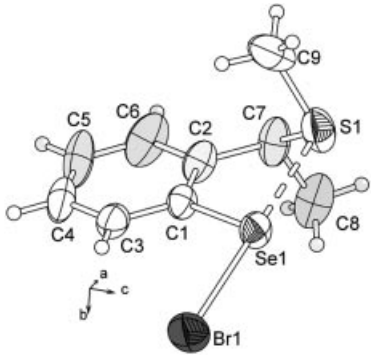


Figure 1. ORTEP drawing and labeling scheme for **2**. Se–S interaction is shown as a dashed line. Ellipsoids are set at 50% probability.

These selenenylating agents were then analyzed in solution by the acquisition of their proton, carbon and selenium NMR spectra in $CDCl_3$. In a first experiment, the Overhauser dipolar correlations for arylselenenyl chloride **3** were measured and compared with those obtained for corresponding arylmethyl selenide **5**. From the results indicated in Scheme 2, it can be deduced that compound **3** presents a greater conformational rigidity than that observed in **5**.

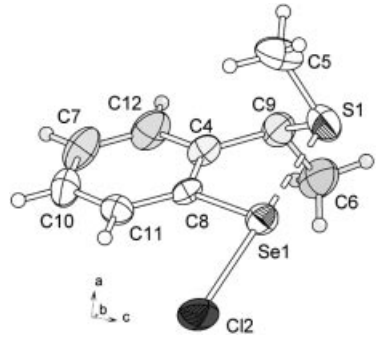


Figure 2. ORTEP drawing and labeling scheme for **3**. Se–S interaction is shown as a dashed line. Ellipsoids are set at 50% probability.

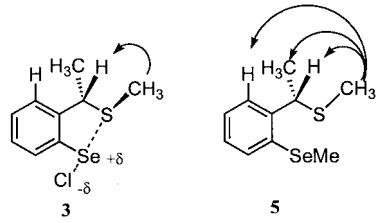
Table 1. Selected bond lengths and angles for compound **2**.

Bond	Distance [Å]	Angle	Amplitude [°]
Se1–S1	2.497(7)	C1–Se1–Br1	98.0(2)
Se1–Br1	2.587(2)	C1–Se1–S1	81.6(2)
Se1–C1	1.880(5)	S1–Se1–Br1	178.8(6)

Table 2. Selected bond lengths and angles for compound **3**.

Bond	Distance [Å]	Angle	Amplitude [°]
Se1–S1	2.344(2)	C8–Se1–Cl2	92.62(9)
Se1–Cl2	2.312(1)	C8–Se1–S1	85.32(9)
Se1–C8	1.929(3)	Cl2–Se1–S1	177.74(4)

This is very likely due to the interaction between the selenium and sulfur atoms, which is not only present in the crystal form, but also present in $CDCl_3$ solutions as well.



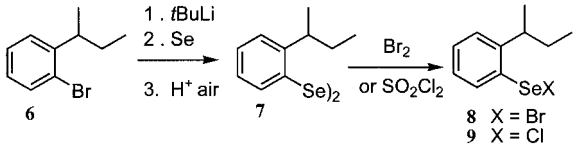
Scheme 2. Main Overhauser correlations for compounds **3** and **5**.

The presence of intramolecular interactions in these compounds can also be deduced from other NMR spectroscopic data.[3,8b,c] Some selected ^{1}H- and ^{13}C NMR chemical shift values (δ_H, δ_C) that were measured for compounds **2**, **3**, and **4** are listed in Table 3. It can be seen that the chemical shifts for the methyl and the methine protons and carbons depend on the electronegativity of the halogen attached to the selenium atom. In agreement with previous observations in other arylselenenyl halides,[3,8b,c] the trend in the chemical shift values is RSeCl > RSeBr > RSeI, and this suggests that the strongest Se–S interaction occurs in the case of chloride **3**.

Table 3. Selected ^{1}H-, ^{13}C- and ^{77}Se NMR δ values for **2**, **3**, and **4** in $CDCl_3$.

Compound	δ_H SCH_3	δ_C SCH_3	δ_H CHS	δ_C CHS	δ_{Se}
Bromide **2**	2.06	18.2	4.27	53.4	750.6
Chloride **3**	2.27	18.5	4.33	54.1	797.3
Iodide **4**	1.90	16.3	4.16	50.8	557

Further evidence came from the analysis of the ^{77}Se NMR spectra. In order to evaluate the influence of the Se–S interaction on the ^{77}Se NMR chemical shift values, *ortho* alkyl-substituted diselenide **7** and the corresponding halogenated derivatives **8** and **9**, in which the sulfur was replaced by a carbon atom, were prepared from bromide **6**[18] according to the synthetic sequence indicated in Scheme 3.



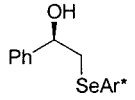
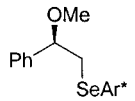
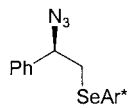
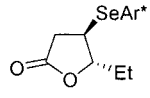
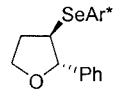
Scheme 3. Synthesis of diselenide **7** and halo derivatives **8** and **9**.

Steric hindrance results in an upfield shift of the ^{77}Se NMR signals of bromide **8** (δ =832 ppm) and chloride **9** (1004 ppm) with respect to unsubstituted PhSeBr (δ =867 ppm) and PhSeCl (1044 ppm). This upfield shift is a result of the Se–S interaction (δ =750 ppm for compound **2** and 797 ppm for compound **3**). This observation is in agreement with the trend observed by Tomoda in the case of Se–O interaction.[3]

Finally, the efficiency of arylselenenyl halides **2**, **3**, and **4** in the promotion of the asymmetric inter- and intramolecular addition to alkenes was explored. For this purpose, some selected hydroxy-, methoxy- and azidoselenenylation reactions, as well as selenoetherification and selenolactonization reactions were effected from alkenes **10a**–**e**. The stereoselectivity of the reactions of **8** and **9** was also examined. The results of these experiments are collected in Table 4. All of the reactions were carried out with a stoichiometric amount of the selenenylating agent at the temperature indicated in Table 4. Complete regioselectivity was observed in every case and only two diastereomers, each of which is constituted by a single enantiomer, were obtained. Excellent levels of diastereoselectivities were obtained in every case. These diastereoselectivities were very similar to those obtained from the same reactions carried out with the selenenyl triflate that is produced in situ from diselenide **1**.[13,12a] In the methoxyselenenylation of styrene carried out with reagents **8** and **9** (Entry b), no diastereoselectivity was observed; the two racemic diastereomers were obtained in equal amounts. This result confirms the importance of the presence of the sulfur heteroatom in the chiral moiety and of its interaction with the electrophilic selenium atom in directing selective attack at the double bond.

The diastereomeric ratios were determined from the analysis of the ^{1}H NMR spectra of the crude reaction mixtures and were then confirmed after the product was purified by column chromatography. The absolute configura-

Table 4. Asymmetric addition reactions promoted by the electrophilic reagents **2**, **3**, **4**, **8**, and **9**.

					Reagent				
					2	**3**	**4**	**8**	**9**
Entry	Alkene **10**	Solvent T [°C]	Nucleophile	Product **11**	*dr* Yield [%]	*dr* Yield [%]	*dr* Yield [%]	*dr* Yield [%]	*dr* Yield [%]
a	styrene	CH_3CN -30	H_2O		95/5 60	93/7 90	92/8 60	–	–
b	styrene	CH_2Cl_2 -30	CH_3OH		97/3 98	95/5 81	92/8 75	50/50 70	50/50 60
c	styrene	CH_3CN -30	NaN_3		92/8 75	–	–	–	–
d	*trans*-3-hexenoic acid	CH_2Cl_2 r.t.	–		97/3 90	86/14 98	73/27 65	–	–
e	*trans*-4-phenyl-3-buten-1-ol	CH_2Cl_2 r.t.	–		93/7 70	91/9 97	92/8 76	–	–

tions reported in Table 4 refer to the major diastereomer and were assigned on the basis of a comparison with the data reported in the literature.[19]

In conclusion, we have reported convincing experimental evidence for the presence of an intramolecular selenium–sulfur interaction in arylselenenyl halides, and we have demonstrated the crucial role of this interaction in the attainment of excellent levels of facial selectivity in several selenium addition reactions.

Experimental Section

General: All new compounds were fully characterized by ^{1}H-, ^{13}C-, and ^{77}Se NMR, mass spectra and elemental analyses. ^{1}H-, ^{13}C-, and ^{77}Se NMR spectra were recorded with a Bruker Avance-DRX 400 instrument. GC–MS analyses were carried out with an HP-6890 gas chromatograph (dimethyl silicone column, 12.5 m) equipped with an HP-5973 mass-selective detector. Optical rotations were measured with a JASCO DIP-1000 digital polarimeter. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. Melting points were determined with a capillary melting point apparatus and are uncorrected. Unless otherwise indicated, all the starting materials are commercially available. Physical and spectroscopic data for all of the new compounds are reported below.

Synthesis of 2-{[(1*S*)-1-Methylthio]-ethyl}phenylselenenyl Bromide (2): To a solution of diselenide **1** (0.460 g, 1 mmol) in diethyl ether (20 mL), a stoichiometric amount of a Br_2 (1 M solution in CCl_4) was added at 0 °C. The reaction mixture was stirred for 30 min and then evaporated under vacuum to afford a deep red solid. Compound **2** was purified by crystallization from diethyl ether. Yield 558 mg, 90%. M.p. 114–116 °C. $[\alpha]_D^{13.7}$ = +237.0 (C = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 8.31 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH*Ar*), 7.30–7.20 (m, 2 H, 2CH*Ar*), 7.12 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, CH*Ar*), 4.27 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, CHS), 2.27 (s, 3 H, SCH_3), 1.75 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 141.2 (C_{ipso}), 134.8 (CH*Ar*), 133.6 (C_{ipso}), 129.6 (CH*Ar*), 127.6 (CH*Ar*), 127.3 (CH*Ar*), 53.8 (CHS), 18.9 (CH_3), 18.4 (SCH_3) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$/TMS, 25 °C): δ = 750.6 ppm. $C_9H_{11}SeBr$ (310.11): calcd. C 34.87, H 3.58; found C 34.33, H 3.22.

Synthesis of 2-{[(1*S*)-1-Methylthio]-ethyl}phenylselenenyl Chloride (3): To a solution of diselenide **1** (0.460 g, 1 mmol) in diethyl ether (20 mL), a stoichiometric amount of SO_2Cl_2 (0.135 g, 1 mmol) was added at 0 °C. The reaction mixture was stirred for 30 min and then evaporated under vacuum to afford an orange solid from which compound **3** was obtained after crystallization from diethyl ether. Yield 478 mg, 90%. M.p. 140–143 °C. $[\alpha]_D^{22.1}$ = +250.0 (C = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 8.32 (dd, $^4J_{H,H}$ = 1.1 Hz, $^3J_{H,H}$ = 8.1 Hz, 1 H, CH*Ar*), 7.33 (ddd, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 8.1 Hz, 1 H, CH*Ar*), 7.24 (dt, $^4J_{H,H}$ = 1.1 Hz, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH*Ar*), 7.16 (dd, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH*Ar*), 4.33 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, CHS), 2.35 (s, 3 H, SCH_3), 1.75 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 140.6 (C_{ipso}), 135.6 (C_{ipso}), 132.5 (CH*Ar*), 129.4 (CH*Ar*), 127.4 (CH*Ar*), 127.2 (CH*Ar*), 54.1 (CHS), 19.0 (CH_3), 18.5 (SCH_3) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$/TMS, 25 °C): δ = 797.3 ppm. $C_9H_{11}SeCl$ (265.66): calcd. C 40.70, H 4.17; found C 41.15, H 4.29.

Synthesis of 2-{[(1*S*)-1-Methylthio]-ethyl}phenylselenenyl Iodide (4): To a solution of diselenide **1** (0.460 g, 1 mmol) in diethyl ether (20 mL), a stoichiometric amount of I_2 (0.1 M solution in CCl_4) was added at 0 °C. The reaction mixture was stirred for 30 min. The resulting solution was evaporated to afford **4** as a red oil. Yield 571 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 8.15 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.30–7.20 (m, 2 H, 2CH*Ar*), 7.07 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, CH*Ar*), 4.16 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 2.06 (s, 3 H, SCH_3), 1.75 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 143.0 (C_{ipso}), 139.3 (CH*Ar*), 130.4 (C_{ipso}), 129.4 (CH*Ar*), 127.9 (CH*Ar*), 127.6 (CH*Ar*), 50.8 (CHS), 18.7 (CH_3), 16.3 (SCH_3) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$/TMS, 25 °C): δ = 557 ppm.

Synthesis of 2-{[(1*S*)-1-Methylthio]-ethyl}phenylmethyl Selenide (5): To a solution of diselenide **1** (0.460 g, 1 mmol) in diethyl ether (25 mL), $LiAlH_4$ (1 M solution in hexane, 0.5 mL, 0.5 mmol) was added at 0 °C. After 15 min, methyl iodide (0.9 mL, 1.5 mmol) was added, and the mixture was stirred for 2 h at room temperature. After the usual workup, the organic layers were dried (Na_2SO_4) and the solvents evaporated under vacuum. The crude product was purified by column chromatography on silica gel with a mixture of diethyl ether and light petroleum ether (50:50) as the eluent to afford **5** as an oil. Yield 392 mg, 80%. $[\alpha]_D^{30.0}$ = –1.20 (C = 0.725, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.55 (dd, $^4J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH*Ar*), 7.48 (dd, $^4J_{H,H}$ = 1.6 Hz, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH*Ar*), 7.31 (ddd, $^4J_{H,H}$ = 1.6 Hz, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH*Ar*), 7.23 (ddd, $^4J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH*Ar*), 4.50 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 2.39 (s, 3 H, $SeCH_3$), 2.03 (s, 3 H, SCH_3), 1.65 (d, $^3J_{H,H}$ = 7.0, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 144.1 (C_{ipso}), 133.0 (C_{ipso}), 130.9 (CH*Ar*), 128.1 (CH*Ar*), 127.3 (CH*Ar*), 127.1 (CH*Ar*), 44.1 (CHS), 22.0 (CH_3), 14.6 (SCH_3), 8.3 ($SeCH_3$) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$/TMS, 25 °C): δ = 156.7 ppm. MS (70 eV, EI): *m*/*z* (%) = 246 (49) $[M]^+$, 244 (25), 231 (88) $[M - CH_3]^+$, 216 (5), 199 (42) $[M - CH_3]^+$, 183 (100) $[C_8H_7Se]^+$, 104 (72), 91 (19), 77 (22), 51 (7).

Synthesis of 2-(2-*sec*-Butyl)phenyl Diselenide (7): To a solution of **6** (1 mmol) in freshly distilled THF, *t*BuLi (1.7 M solution in pentane, 1.5 mmol) was added at –78 °C. After 3 h, the temperature was raised to 0 °C, and the mixture was stirred for an additional 30 min. Elemental selenium was added (1.5 mmol), and the reaction mixture was stirred for 3 h at room temperature. The resulting solution was poured into HCl (7%) and was stirred overnight at room temperature. After filtration, the aqueous layer was extracted twice with ether, and the combined organic layers were dried with Na_2SO_4 and the solvents evaporated under vacuum to afford a crude product which was purified by flash chromatography on a silica gel column with light petroleum ether as the eluent. Diselenide **7** was obtained as an oil and as an equimolecular mixture of *syn* and *anti* diastereomers which could not be separated. Yield 170 mg, 80%. MS (70 eV, EI): *m*/*z* (%) = 426 (100) $[M]^+$, 424 (92), 345 (6), 212 (57), 197 (36), 183 (46), 157 (25), 155 (12), 132 (18), 117 (31), 91 (47), 77 (14), 55 (15).

Synthesis of 2-(2-*sec*-Butyl)phenylselenenyl Bromide (8) and 2-(2-*sec*-Butyl)phenylselenenyl Chloride (9): Compounds **8** and **9** were synthesized from **7** with the same procedure employed for **2** and **3**.

8: Oil. Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.92 (dd, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.43 (dt, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.3 Hz, 1 H, CH*Ar*), 7.20 (ddd, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 3.39 (sext, $^3J_{H,H}$ = 7.0 Hz, 1 H, CH), 1.67 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 1.29 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.88 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 151.0 (C_{ipso}), 137.1 (CH*Ar*), 131.5 (CH*Ar*), 130.3 (C_{ipso}),

126.9 (CH*Ar*), 126.5 (CH*Ar*), 40.8 (CH), 31.1 (CH_2), 22.0 (CH_3), 12.2 (CH_3) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$/TMS, 25 °C): δ = 832.5 ppm.

9: Oil. Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 8.23 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.61 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.53 (ddd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.42 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 2.94 (sext, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH), 1.80–1.70 (m, 2 H), 1.36 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 0.89 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 147.7 (C_{ipso}), 146.5 (C_{ipso}), 134.2 (CH*Ar*), 128.4 (CH*Ar*), 127.5 (CH*Ar*), 124.5 (CH*Ar*), 39.7 (CH), 31.4 (CH_2), 22.3 (CH_3), 12.7 (CH_3) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$/TMS, 25 °C): δ = 1004.1 ppm.

Hydroxyselenenylation of Styrene: To a solution of chiral electrophilic selenenylating reagents **2**, **3**, or **4** (1 mmol) in CH_3CN, styrene (1 mmol) dissolved in a mixture of CH_3CN/H_2O (2:1) was added at –30 °C. The resulting solution was stirred for 3 d. The progress of the reaction was monitored by GC–MS and TLC. The reaction mixture was then poured into a solution of $NaHCO_3$ (10%) and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and the solvents evaporated under vacuum. The products were purified by flash chromatography on a silica gel column with a mixture of diethyl ether and light petroleum ether (1:9) as the eluent. The reaction yields and the diastereomeric ratios (*dr*) are reported in Table 4.

(1*R*)-2-{2-[(1*S*)-1-(Methylthio)ethyl]phenylseleneny}-1-phenylethanol (11a): Major isomer: Oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.61 (dd, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.5 Hz, 1 H, CH*Ar*), 7.50 (dd, $^4J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.38 (m, 6 H, 6CH*Ar*), 7.21 (dt, $^4J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 4.76 (dd, $^3J_{H,H}$ = 3.5 Hz, $^3J_{H,H}$ = 9.6 Hz, 1 H, C*H*OH), 4.55 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 3.38 (dd, $^3J_{H,H}$ = 3.5 Hz, $^2J_{H,H}$ = 12.6 Hz, 1 H, CH*H*Se), 3.10 (dd, $^3J_{H,H}$ = 9.6 Hz, $^2J_{H,H}$ = 12.6 Hz, 1 H, C*H*HSe), 3.00 (s, 1 H, OH), 2.02 (s, 3 H, SCH_3), 1.65 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 150.9 (C_{ipso}), 145.1 (C_{ipso}), 134.0 (CH*Ar*), 130.2 (C_{ipso}), 128.5 (2CH*Ar*), 127.9 (CH*Ar*), 127.8 (CH*Ar*), 127.6 (CH*Ar*), 127.1 (CH*Ar*), 125.7 (2CH*Ar*), 72.5 (CHOH), 44.1 (CHS), 38.9 (CH_2Se), 21.3 (CH_3), 14.0 (SCH_3) ppm. MS (70 eV, EI): *m*/*z* (%) = 352 (10) $[M]^+$, 231 (59), 229 (30), 185 (21), 183 (100), 181 (52), 103 (20), 91 (25), 77 (24). IR (neat): $\tilde{\nu}$ = 3200 (OH) cm^{-1}.

Methoxyselenenylation of Styrene: To a solution of chiral electrophilic selenenylating reagents **2**, **3**, **4**, **8**, or **9** (1 mmol) in CH_2Cl_2, styrene (1 mmol) dissolved in MeOH was added at –30 °C. The resulting solution was stirred for 3 d. The progress of the reaction was monitored by GC–MS and TLC. The reaction mixture was then poured into a solution of $NaHCO_3$ (10%) and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and evaporated in vacuo. The products were separated by flash chromatography on a silica gel column with a mixture of diethyl ether and light petroleum ether (7:93) as the eluent. The reaction yields and the diastereomeric ratios are reported in Table 4.

1-{[(2*R*)-2-Methoxy-2-phenylethyl]selenenyl}-2-[(1*S*)-1-(methylthio)ethyl]benzene (11b): Oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.51 (dd, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.48 (dd, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.40–7.30 (m, 5 H, 5CH*Ar*), 7.26 (dt, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.12 (dt, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 4.58 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 4.35 (dd, $^3J_{H,H}$ = 4.9 Hz, $^3J_{H,H}$ = 8.7 Hz, 1 H, $CHOCH_3$), 3.30 (dd, $^3J_{H,H}$ = 8.7 Hz, $^2J_{H,H}$ = 12.1 Hz, 1 H, CH*H*Se), 3.10 (dd, $^3J_{H,H}$ = 4.9 Hz, $^2J_{H,H}$ = 12.1 Hz, 1 H, C*H*HSe), 3.26 (s, 3 H, OCH_3), 1.95 (s, 3 H, SCH_3), 1.57 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 144.9 (C_{ipso}), 140.8 (C_{ipso}), 133.3 (CH*Ar*), 131.5 (C_{ipso}), 128.5 (2CH*Ar*), 128.0 (CH*Ar*), 127.4 (CH*Ar*), 127.3 (CH*Ar*), 126.8 (CH*Ar*), 126.5 (2CH*Ar*), 82.9 ($CHOCH_3$), 56.9 (OCH_3), 43.8 (CHS), 35.8 (CH_2Se), 21.4 (CH_3), 14.0 (SCH_3) ppm. MS (70 eV, EI): *m*/*z* (%) = 366 (23) $[M]^+$, 364 (12), 231 (79), 183 (100) $[ArSe]^+$, 135 (28), 121 (67), 103 (27), 91 (31), 77 (22), 61 (6), 51 (4).

Azidoselenenylation of Styrene: To a solution of reagent **2** (1 mmol) in $CH_3CN{\cdot}NaN_3$ (1 mmol) was added at –30 °C. The reaction mixture was stirred for 30 min, and styrene (1.0 mmol) was then added. The reaction was warmed to room temperature, and the reaction was then stirred for 3 d. The progress of the reaction was monitored by ^{1}H NMR and TLC. After the usual workup, the mixture was filtered through anhydrous K_2CO_3, and the solvents were evaporated under vacuum. The products were separated by flash chromatography on a silica gel column with a mixture of diethyl ether and light petroleum ether (1:9) as the eluent. The yield and the diastereomeric ratio are reported in Table 4.

1-{[(2*R*)-2-Azido-2-phenylethyl}selenenyl]-2-[(1*S*)-1-(methylthio)-ethyl]benzene (11c): Oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.51 (dd, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.52 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CH*Ar*), 7.38 (dt, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.19 (dt, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CH*Ar*), 4.57 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 4.38 (ddd, $^3J_{H,H}$ = 4.4 Hz, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CHO), 3.60 (ddd, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 8.4 Hz, 1 H, CHSe), 3.30 (dd, $^3J_{H,H}$ = 8.4 Hz, $^2J_{H,H}$ = 16.1 Hz, 1 H, C*H*HCO), 2.62 (dd, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 16.1 Hz, 1 H, CH*H*CO), 1.99 (s, 3 H, SCH_3), 1.60 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.80–1.70 (m, 1 H, CH*H*CH_3), 1.65–1.60 (m, 1 H, C*H*HCH_3), 0,96 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 148.5 (C_{ipso}), 142.1, 133.8, 131.2, 129.9, 127.9, 127.7, 127.6, 127.3, 124.6, 69.9 (CHN_3), 47.7 (CHS), 31.2 (CH_2Se), 22.4 (CH_3), 14.5 (SCH_3) ppm. IR (neat): $\tilde{\nu}$ = 2090 cm^{-1} (N_3).

General Procedure for the Cyclofunctionalization Reactions: To a solution of chiral electrophilic selenenylating reagent **2**, **3**, or **4** (1 mmol) in CH_2Cl_2, alkene **10d** or **10e** (1 mmol) dissolved in CH_2Cl_2 and $NaHCO_3$ (2 mmol) were added at room temperature. The reaction mixture was stirred for 3 d. The progress of the reaction was monitored by GC–MS and TLC. The reaction mixture was then poured into a solution of $NaHCO_3$ (10%) and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and the solvents evaporated. The products were purified by flash chromatography on a silica gel column with a mixture of diethyl ether and light petroleum ether (7:93) as the eluent. The yields and the diastereomeric ratios are reported in Table 4.

(4*R*,5*S*)-5-Ethyl-4-{2-[(1*S*)-1-(methylthio)ethyl]phenylselenenyl}-dihydrofuran-2(3*H*)-one (11d): Oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.57 (dd, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.52 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CH*Ar*), 7.38 (dt, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 7.6 Hz, 1 H, CH*Ar*), 7.19 (dt, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CH*Ar*), 4.57 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 4.38 (ddd, $^3J_{H,H}$ = 4.4 Hz, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CHO), 3.60 (ddd, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 8.4 Hz, 1 H, CHSe), 3.30 (dd, $^3J_{H,H}$ = 8.4 Hz, $^2J_{H,H}$ = 16.1 Hz, 1 H, C*H*HCO), 2.62 (dd, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 16.1 Hz, 1 H, CH*H*CO), 1.99 (s, 3 H, SCH_3), 1.60 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.80-1.70 (m, 1 H, CH*H*CH_3), 1.65–1.60 (m, 1 H, C*H*HCH_3), 0.96

(t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 174.6 (CO), 146.5 (C_{ipso}), 136.3 (C_{ipso}), 130.3 (CH*Ar*), 129.3 (CH*Ar*), 127.7 (CH*Ar*), 127.4 (CH*Ar*), 87.3 (CHO), 44.0 (CHS), 39.1 (CHSe), 36.3 (CH_2), 27.0 (CH_2), 21.2 (CH_3), 13.9 (SCH_3), 9.6 (CH_3) ppm. MS (70 eV, EI): *m/z* (%) = 344 (1) $[M]^+$, 232 (13), 230 (58), 229 (25), 185 (20), 183 (100) $[ArSe]^+$, 180 (22), 104 (12), 91 (10).

(2*S*,3*R*)-3-{2-[(1*S*)-1-(Methylthio)ethyl]phenylselenenyl}-2-phenyltetrahydrofuran (11e): Oil. ^1H NMR (400 MHz, $CDCl_3$/TMS, 25 °C): δ = 7.49 (dd, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH*Ar*), 7.48 (dd, $^3J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CH*Ar*), 7.33-7.25 (m, 6 H, 6CH*Ar*), 7.08 (dt, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CH*Ar*), 4.87 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, PhCHO), 4.58 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHS), 4.20 (dt, $^3J_{H,H}$ = 4.9 Hz, $^2J_{H,H}$ = $^3J_{H,H}$ = 8.2 Hz, 1 H, CH*H*O), 4.15 (dt, $^3J_{H,H}$ = 7.4 Hz, $^2J_{H,H}$ = $^3J_{H,H}$ = 8.2 Hz, 1 H, C*H*HO), 3.60 (dt, $^3J_{H,H}$ = 6.0 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, CHSe), 2.50–2.40 (m, 1 H, CH*H*), 2.20–2.10 (m, 1 H, C*H*H), 2.0 (s, 3 H, SCH_3), 1.50 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$/TMS, 25 °C): δ = 145.3 (C_{ipso}), 140.8 (C_{ipso}), 134.8 (CH*Ar*), 129.9 (C_{ipso}), 127.9 (CH*Ar*), 127.8 (2CH*Ar*), 125.3 (CH*Ar*), 126.9 (CH*Ar*), 126.6 (CH*Ar*), 125.4 (2CH*Ar*), 85.8 (OCHPh), 67.6 (OCH_2), 47.9 (CHSe), 43.5 (CHS), 33.6 (CH_2), 21.0 (CH_3), 13.6 (SCH_3) ppm. MS (70 eV, EI): *m/z* (%) = 378 (1) $[M]^+$, 231 (49), 229 (27), 183 (93), 147 (100), 105 (37), 91 (31), 77 (19).

Acknowledgments

Financial support from MIUR, National Projects COFIN2003 and FIRB2001, and Consorzio CINMPIS is gratefully acknowledged.

[1] a) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**; b) L. Gonzalez, O. Mo, M. Yanez "Protonation and Deprotonation of Thiomalonaldehyde. The Role of the Intramolecular Hydrogen Bond" in *Recent Theoretical and Experimental Advances in Hydrogen bonded Clusters* (Ed.: S. S. Xantheas), Kluwer, Dordrecht, **2000**; c) J. Emsley, *Structure and Bonding*, Springer, Berlin, **1984**.

[2] a) M. J. Frisch, A. C. Scheiner, H. F. Schaefer III, J. S. Binkley, *J. Chem. Phys.* **1985**, *82*, 4194; b) F. Sim, A. St-Amant, I. Papai, D. R. Salahub, *J. Am. Chem. Soc.* **1992**, *114*, 4391; c) Z. Latajka, S. Scheiner, *J. Phys. Chem.* **1992**, *96*, 9764; d) D. C. Mulhearn, S. Bachrach, *J. Org. Chem.* **1995**, *60*, 7110; e) V. Barone, C. Adamo, *J. Chem. Phys.* **1996**, *105*, 11007; f) P. Sanz, M. Ynez, O. Mò, *Chem. Eur. J.* **2003**, *9*, 4548.

[3] a) M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* **2004**, *126*, 5309.

[4] a) B. M. Goldstein, S. D. Kennedy, W. J. Hemnen, *J. Am. Chem. Soc.* **1990**, *112*, 8285; b) D. H. R. Barton, M. B. Hall, Z. Lin, S. I. Pareck, J. Reibenspies, *J. Am. Chem. Soc.* **1993**, *115*, 5056; c) V. N. Ramasubbu, R. Parthasarathy, *Phosphorus Sulfur* **1987**, *31*, 221.

[5] I. Hargittai, B. Rozsondai, "Structural Chemistry of Organic Compounds Containing Selenium or Tellurium" in *The Chemistry of Organic Selenium and Tellurium Compounds* (Eds.: S. Patai, Z. Rappoport), John Wiley & Sons, New York, **1986**, vol. 1.

[6] a) M. Baiwir, G. Llabres, O. Dideberg, L. Dupont, J.-L. Piette, *Acta Crystallogr., Sect. B* **1975**, *31*, 2188; b) H. W. Roesky, K.-L. Weber, U. Seseke, W. Pinkert, M. Noltemeyer, W. Clegg, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1985**, 565; c) S. Tomoda, M. Iwaoka, K. Yakushi, A. Kawamoto, J. Tanaka, *J. Phys. Org. Chem.* **1988**, *1*, 179; d) S. Tomoda, M. Iwaoka, *J. Chem. Soc., Chem. Commun.* **1990**, 231; e) S. Kubiniok, W.-W. du Mont, S. Pohl, W. Saak, *Angew. Chem. Int. Ed.* **1988**, *27*, 431; f) W.-W. du Mont, A. Martens, S. Pohl, W. Saak, *Inorg. Chem.* **1990**, *29*, 4847.

[7] a) F. T. Burling, B. M. Goldstein, *J. Am. Chem. Soc.* **1992**, *114*, 2313; b) M. Iwaoka, S. Tomoda, *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *67*, 125; c) M. Iwaoka, S. Tomoda, *J. Org. Chem.* **1995**, *60*, 5299.

[8] a) M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* **2004**, *126*, 5309; b) G. Mugesh, A. Panda, H. B. Singh, R. J. Butcher, *Chem. Eur. J.* **1999**, *5*, 1411; c) M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.* **1996**, *118*, 8077.

[9] a) M. Tiecco, "Electrophilic Selenium, Selenocyclizations" in *Topics in Current Chemistry: Organoselenium Chemistry – Modern Developments in Organic Synthesis* (Eds.: T. Wirth), Springer-Verlag, Heidelberg, **2000**, pp. 7–54; b) T. G. Back (Ed.), *Organoselenium Chemistry – A Practical Approach*, Oxford, New York, **2000**; c) T. Wirth, *Angew. Chem. Int. Ed.* **2000**, *39*, 3742; d) M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Tetrahedron: Asymmetry* **2000**, *11*, 4645; e) M. Tiecco, L. Testaferri, F. Marini, S. Sternativo, A. Temperini, L. Bagnoli, C. Santi, *Tetrahedron: Asymmetry* **2001**, *12*, 1493; f) M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Eur. J. Org. Chem.* **2000**, 3451.

[10] a) T. Wirth, G. Fragale, M. Spichty, *J. Am. Chem. Soc.* **1998**, *120*, 3376; b) X. Wang, K. N. Houk, M. Spichty, T. Wirth, *J. Am. Chem. Soc.* **1999**, *121*, 8567; c) M. Spichty, G. Fragale, T. Wirth, *J. Am. Chem. Soc.* **2000**, *122*, 10914.

[11] a) M. Iwaoka, H. Komatsu, T. Kotsuda, S. Tomoda, *J. Am. Chem. Soc.* **2002**, *124*, 1902; b) M. Iwaoka, T. Kotsuda, H. Komatsu, S. Tomoda, *J. Org. Chem.* **2005**, *70*, 321; c) M. Iwaoka, S. Tomoda, *Phosphorous, Sulfur Silicon Relat. Elem.* **2005**, *180*, 755.

[12] a) M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Angew. Chem. Int. Ed.* **2003**, *42*, 3131; b) M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Chem. Eur. J.* **2002**, *8*, 1118; c) M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, R. Bonini, F. Marini, L. Bagnoli, A. Temperini, *Org. Lett.* **2004**, *6*, 4751.

[13] M. Tiecco, L. Testaferri, L. Bagnoli, F. Marini, A. Temperini, C. Tomassini, C. Santi, *Tetrahedron Lett.* **2000**, *41*, 3241.

[14] Single crystal diffraction data collection for **2** and **3** was carried out with an XCALIBUR Oxford Instruments diffractometer equipped with a CCD detector, with graphite monochromated Mo-K_α radiation and operating at 50 kV and 30 mA. To maximize the reciprocal space coverage, a combination of ω and φ scans was used with a step-size of 0.5° and a time of 30 s/frame. The distance between the crystal and the detector was 60.4 mm. Data were corrected for absorption with the SADABS program.[20] The structure was solved by direct methods (SIR 97 program[21]) and refined by full-matrix least-squares against F^2 with the use of all data and with the use of the SHELXTL software package.[22] Non-H atoms were refined anisotropically; H atoms were placed in calculated positions. Absolute structure configuration for both structures was tested with the Flack test and the Flack parameters were 0.01(1) and 0.02(1) for **2** and **3**, respectively.[23] Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC-294258 and -294259 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. *Crystal data for 2*: $C_9H_{10}Br_1S_1Se_1$, FW = 309.10, monoclinic, space group $P2_1$ (no. 4), Z = 2, a = 11.048(2), b = 9.118(1), c = 11.081(2) Å, β = 92.440(3)°, V = 1115.2(9) Å^3, $\rho_{calcd.}$ = 1.84 g cm^{-3}, μ(Mo-K_α) = 7.084 mm^{-1}, F(000) = 752; 5764 data ($2\theta_{max}$ = 50°) of which 4254 unique, R_{int} = 0.017; 213 parameters, [a] wR_2 = 0.055, [b] S = 1.016 (all data), [c] R_1 [2866 with $I > 2\sigma(I)$] = 0.029, largest final difference peak/hole +0.38/–0.31 e·Å^{-3}.

[15] *Crystal Data for 3*: $C_9H_{10}Cl_1S_1Se_1$, FW = 264.64, orthorhombic, space group $P\,2_12_12_1$ (no. 19), $Z = 4$, $a = 8.391(1)$, $b = 10.849(1)$, $c = 11.011(1)$ Å, $V = 1002.4(9)$ Å^3, $\rho_{calcd.} = 1.75$ g cm^{-3}, μ(Mo-K_α) = 4.162 mm^{-1}, $F(000) = 524$; 4360 data ($2\theta_{max} = 50°$), of which 1742 unique, $R_{int} = 0.021$; 109 parameters, $wR_2 = 0.049$, $S = 1.001$ (all data), R_1 [1610 with $I > 2\sigma(I)$] = 0.023, largest final difference peak/hole +0.29/–0.30 e·Å^{-3}.
[16] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
[17] The covalency factor χ for the intramolecular Se–S interaction can be estimated by the following equation: $\chi = [(R_{Se} + R_S)_{vdW} - d_{SeS}]/[(R_{Se} + R_S)_{vdW} - (r_{Se} + r_S)_{cov}]$ where R and r are the van der Waals and the covalent radii, respectively, and d the distance between the two interacting atoms.
[18] a) G. R. Van Hecke, W. D. Horrocks, *Inorg. Chem.* **1966**, *5*, 1968; b) G. S. Reddy, W. Tam, *Organometallics* **1984**, *3*, 630.
[19] M. Tiecco, L. Testaferri, L. Bagnoli, F. Marini, A. Temperini, C. Tomassini, C. Santi, *Tetrahedron Lett.* **2000**, *41*, 3241.
[20] G. M. Sheldrick, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany, **1996**b.
[21] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
[22] G. M. Sheldrick, *SHELXL-97 – Program for Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
[23] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876.

Received: May 9, 2006
Published Online: August 24, 2006

