New Selenosemicarbazides Derived from Imidazole-Based Carbohydrazides

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Imidazole-based carbohydrazides, *i.e.*, 3-oxidoimidazole-4-carbohydrazides **1** and 2-[(imidazol-2-yl)sulfanyl]acetohydrazides **6**, react with aryl isoselenocyanates **4** in MeOH at room temperature to give the corresponding selenosemicarbazides **5** and **7**, respectively, in good yields. On heating **7b** in DMF in the presence of air to 100°, 1,3,4-oxadiazole **8a** was formed *via* cyclization and formal elimination of H_2Se. Product **8a** was also obtained after heating of a mixture of **4a** and **6b** under the same conditions. On the other hand, on heating of a solution of **7c** in MeOH at reflux, a cyclization occurred to give the corresponding 1,2,4-triazole-3-selone **9b**. Again, the same product was formed when a mixture of **4b** and **6b** was heated in MeOH. Surprisingly, analogous cyclizations of selenosemicarbazides of type **5** under the same conditions failed, and only decomposition was observed. The structures of **7a**, **7d**, and **9b** have been established by X-ray crystallography.

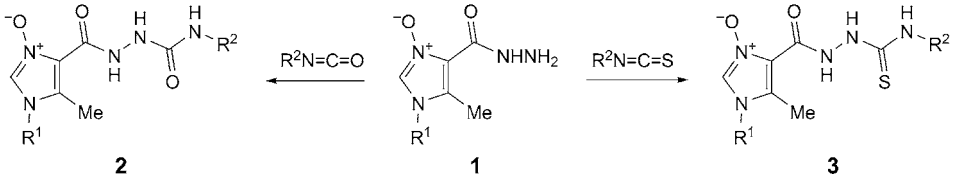
1. Introduction. – Isoselenocyanates are well-known as versatile building blocks for the preparation of linear and cyclic selenoorganic compounds [1]. It is also well-documented that many Se-containing products display diverse biological activities, and some are of significant importance in the pharmaceutical and agrochemical fields [2]. In analogy to isocyanates and isothiocyanates, isoselenocyanates easily react with N-nucleophiles, such as primary and secondary amines, furnishing the corresponding selenoureas [1][3]. Hydrazines display a similar reactivity leading to selenosemicarbazides [4]. In the case of carbohydrazides, only a few reactions with isoselenocyanates have been reported to date [4a][4b][5]. Whereas, to the best of our knowledge, carbohydrazides derived from heterocyclic carboxylic acids have not yet been used in such reactions [6], reactions of benzohydrazide with aliphatic and aromatic isoselenocyanates are known [4a][4c], and, in a recent study, selenosemicarbazides obtained thereby were shown to form 1,3,4-oxadiazole derivatives upon heating in DMF solution to 100° in the presence of air O_2 [5]. This reaction was accompanied by the formation of elemental Se. Other reactions aimed at the synthesis of Se-containing heterocycles starting with selenosemicarbazides have not been described so far.

In a series of recent publications, we reported on the preparation and some reactions of imidazole-based carbohydrazides. For example, carbohydrazides of 3-

[1]) In part from the Ph.D. thesis of *A. M. P.*, University of Łódź, 2012.
[2]) In part from the Diploma thesis of *K. C.*, University of Łódź, 2007.
[3]) Dr. *Z. Cebulska* passed away on August 8, 2007.

oxido-1*H*-imidazole-4-carboxyhydrazide **1** reacted with isocyanates and isothiocyanates leading to semicarbazides **2** and thiosemicarbazides **3**, respectively, in good yields [7] (*Scheme 1*). Both types of products were subsequently used as starting materials for the preparation of bis-heterocyclic systems.

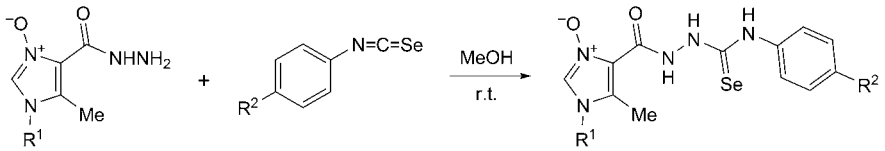
Scheme 1



The aim of the present study was the synthesis of new selenosemicarbazides derived from imidazole-carbohydrazides and their potential application for the preparation of Se-containing bis-heterocyclic products.

2. Results and Discussion. – The starting carbohydrazides of type **1** are conveniently accessible *via* cyclocondensation of α-hydroxyimino β-keto esters with formaldimines and subsequent treatment of the 3-oxidoimidazole-4-carboxylates with $NH_2NH_2 \cdot H_2O$ [7b]. Under standard conditions, the carbohydrazides **1** are stable, crystalline materials. The reactions of **1** with aryl isoselenocyanates **4** were performed at room temperature in MeOH under light protection. In all cases, selenosemicarbazides **5** were isolated after *ca*. 2 d as crystalline materials in good yields (*Scheme 2*).

Scheme 2



1a R^1 = Me
1b R^1 = Bn

4a R^2 = F
4b R^2 = MeO
4c R^2 = H

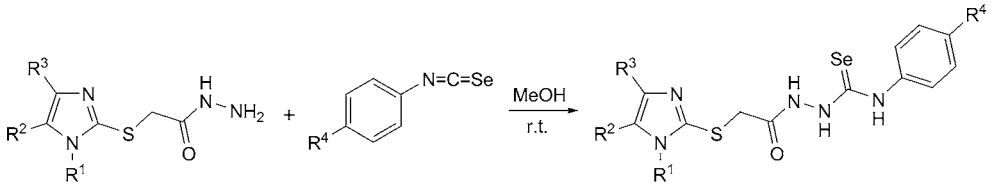
5a R^1 = Me, R^2 = F
5b R^1 = Me, R^2 = MeO
5c R^1 = Bn, R^2 = F
5d R^1 = Bn, R^2 = H

The spectroscopic data confirmed the expected structures. For example, in the case of **5a**, the characteristic ^{1}H-NMR absorption of H–C(2) was observed at 8.48 ppm, indicating a 2-unsubstituted imidazole *N*-oxide. The CONH group absorbed at 1671 cm^{-1} in the IR spectrum, and the corresponding signal in the ^{13}C-NMR spectrum appeared at 179.4 ppm. In addition, the C=Se signal was found at 159.9 ppm. The HR-ESI-MS showed the typical pattern for Se-containing substances with *m*/*z* 372.0367 ($[M+H]^+$). These data evidence that the reactions occurred *via* nucleophilic attack of the hydrazide NH_2 group on the isoselenocyanate, and the *N*-oxide function is preserved under the reaction conditions.

In an extension of the study, hydrazides of type **6** were used for the reactions with **4**. These hydrazides were prepared *via* alkylation of enolizable imidazole-2-thiones with

2-bromoethanoates [8]. The esters obtained thereby were converted to the hydrazides by standard treatment with excess $NH_2NH_2 \cdot H_2O$ [7b]. The reactions of **6** with **4** were also carried out in MeOH at room temperature to yield crystalline products in all cases. The structures of the formed selenosemicarbazides **7** were established by the spectroscopic data (*Scheme 3*). The ^{1}H-NMR spectra revealed the presence of the SCH_2CO fragment by an absorption at 3.95 – 3.45 ppm. In analogy to compounds **5**, the C=Se and C=O resonances in the ^{13}C-NMR spectra appeared at *ca.* 180 and 160 ppm, respectively. In the cases of **7a** and **7d**, single crystals suitable for X-ray crystallography were obtained, and the molecular structures of these compounds were unambiguously confirmed (*cf.* the *Table* in the *Exper. Part*).

Scheme 3



6a $R^1 = R^2 = R^3 =$ Me
6b R^1 = Me, $R^2 = R^3$ = Ph
6c $R^1 = R^2$ = Me, R^3 = Ph
6d R^1 = Bn, $R^2 = R^3$ = Me

4a R^4 = F
4b R^4 = MeO

7a $R^1 = R^2 = R^3$ = Me, R^4 = MeO
7b R^1 = Me, $R^2 = R^3$ = Ph, R^4 = F
7c R^1 = Me, $R^2 = R^3$ = Ph, R^4 = MeO
7d $R^1 = R^2$ = Me, R^3 = Ph, R^4 = MeO
7e $R^1 = R^2$ = Me, R^3 = Ph, R^4 = F
7f R^1 = Bn, $R^2 = R^3$ = Me, R^4 = F
7g R^1 = Bn, $R^2 = R^3$ = Me, R^4 = MeO

The molecular structure of **7d** is shown in *Fig. 1.* The asymmetric unit contains a single molecule. All three NH groups are involved in H-bonds. H–N(20) forms a weak

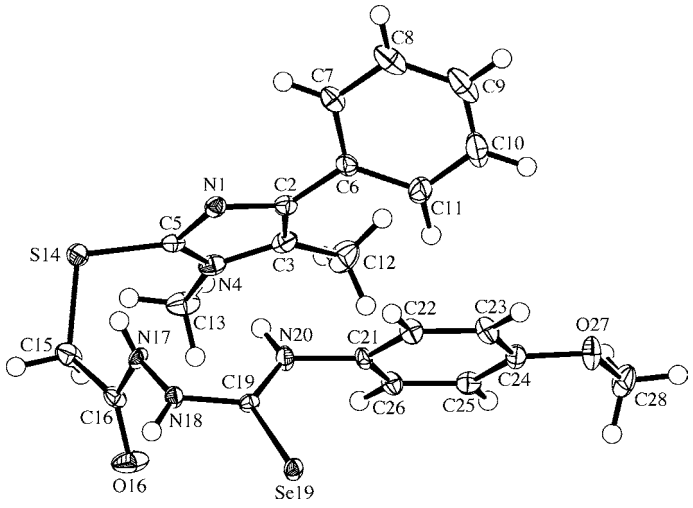


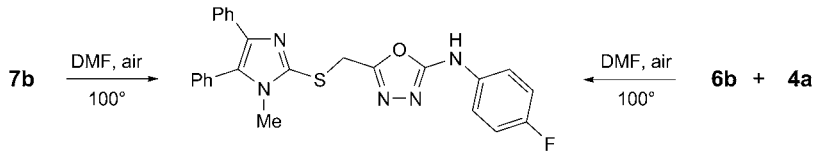
Fig. 1. *ORTEP Plot* [9] *of the molecular structure of* **7d** (50% probability ellipsoids; arbitrary numbering of the atoms; the MeOH molecule is not shown)

intramolecular H-bond with the unsubstituted N(1)-atom in the five-membered ring. This interaction creates a loop which can be described by a graph set motif [10] of $S(10)$. H–N(17) forms an intermolecular H-bond with the same acceptor atom (N(1)) in an adjacent molecule related to the donor molecule by a center of inversion. Therefore, this interaction links pairs of molecules into dimers and can be described by a graph set motif of $R_2^2(14)$. H–N(18) forms an intermolecular H-bond with the Se-atom in a different adjacent molecule which is also related to the donor molecule by a center of inversion. This interaction also links pairs of molecules and can be described by a graph set motif of $R_2^2(8)$. The combination of the intermolecular interactions links the molecules into extended chains, which run parallel to the [110] direction.

The molecular structure of **7a** is quite similar to that of **7d**, but there are two symmetry-independent molecules, A and B, of **7a** and one disordered molecule of $CHCl_3$ in the asymmetric unit. The space group of **7a** is centrosymmetric. For convenience, the asymmetric unit was chosen such that molecule B is related to molecule A by a non-crystallographic center of inversion at (0.24, 0.0, 0.25). The two independent molecules have very similar conformations with an r.m.s. fit of 0.084 Å between the non-H-atoms of molecule A and the inverted atoms of molecule B. The H-bonding pattern and motifs in **7a** are the same as those observed in **7d**, except that, where the intermolecular interactions in **7d** link molecules across crystallographic centers of inversion to form the extended chains, the interactions in **7a** link molecules A and B in an alternating fashion across non-crystallographic centers of inversion to give extended chains which run parallel to the [100] direction.

Both types of selenosemicarbazides, **5** and **7**, are stable at room temperature in the crystalline state as well as in solution. Prompted by recently published results [5], we selected **7b** for the attempted thermal formation of the corresponding 1,3,4-oxadiazole derivatve **8a** (*Scheme 4*). Thus, a solution of **7b** in dry DMF was heated to 100° under an air atmosphere. After 6 h, the ^{1}H-NMR spectra evidenced the disappearance of the starting material and the presence of a new product. The same product was obtained when a mixture **4a**/**6b** was heated in DMF under air for 6 h[4]).

Scheme 4



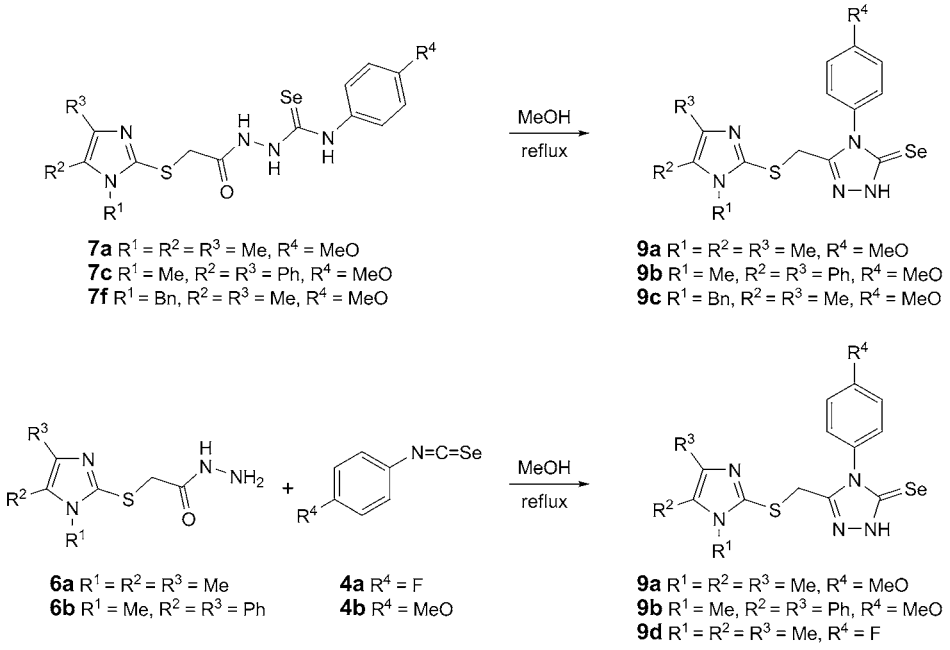
8a

To check whether the formation of Se-containing products from **5** and **7** is possible, solutions of **5b** and **7c** in MeOH were heated at reflux. Under these conditions, after 4 h, **7c** was completely converted to a new compound, which was isolated as a crystalline material in 57% yield. The ESI-MS exhibited the $[M + H]^+$ peak at m/z 534, which corresponds to the molecular formula $C_{16}H_{19}N_5OSSe$, differing from that of **7c**

[4]) The analogous experiments with **5a** and **1a** + **4a**, respectively, failed, and only decomposition and formation of Se was observed.

by elimination of H_2O. The IR spectrum indicated that the new product does not contain a C=O group. The ^{13}C-NMR signal at 160.3 ppm suggested the preservation of the selenourea moiety. Based on these data, the structure of 1,2,4-triazole-3-selone **9b** is proposed (*Scheme 5*)[5]). The same product was obtained from **6b** and **4b** in boiling MeOH. Finally, crystals of **9b** suitable for a crystal-structure determination were obtained from MeOH, and the structure of **9b** was established (*Fig. 2*).

Scheme 5



7a $R^1 = R^2 = R^3 = Me$, $R^4 = MeO$
7c $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = MeO$
7f $R^1 = Bn$, $R^2 = R^3 = Me$, $R^4 = MeO$

9a $R^1 = R^2 = R^3 = Me$, $R^4 = MeO$
9b $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = MeO$
9c $R^1 = Bn$, $R^2 = R^3 = Me$, $R^4 = MeO$

6a $R^1 = R^2 = R^3 = Me$
6b $R^1 = Me$, $R^2 = R^3 = Ph$

4a $R^4 = F$
4b $R^4 = MeO$

9a $R^1 = R^2 = R^3 = Me$, $R^4 = MeO$
9b $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = MeO$
9d $R^1 = R^2 = R^3 = Me$, $R^4 = F$

The asymmetric unit contains one molecule of **9b** plus one molecule of MeOH. The crystal was of poor quality and produced very broad reflection profiles. Consequently, the *R*-factor remains high and the precision of the geometric parameters is low. Nonetheless, the overall structure of the molecule is unambiguous. The space group is non-centrosymmetric, but the presence of mirror or glide planes dictates that the compound in the crystal is racemic. The absolute structure has been determined by the diffraction experiment. The intermolecular H-bonds N(3)–H$\cdots$O(2′) and O(2)–H$\cdots$N(5) link the molecules **9b** and the MeOH molecule in an alternating fashion into extended chains, which run parallel to the [001] direction and have a graph set motif of $C_2^2(10)$.

3. Conclusions. – In the present study, we showed that imidazole-based carbohydrazides **1** and **6** react smoothly with aromatic isoselenocyanates **4** to yield the

[5]) The analogous reactions with **5b** failed.

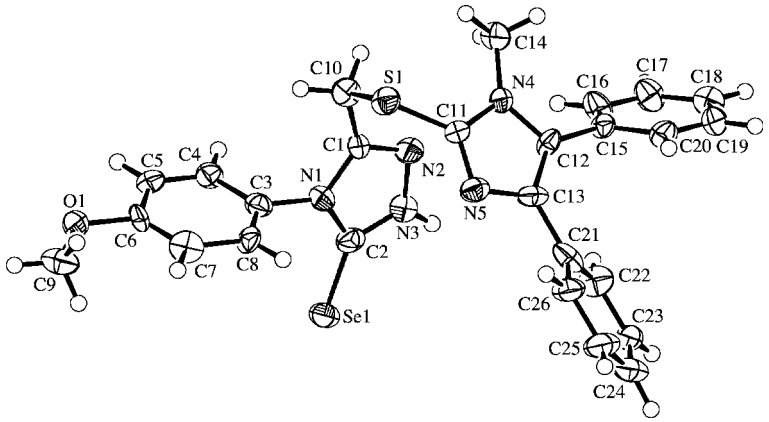


Fig. 2. *ORTEP Plot* [9] *of the molecular structure of* **9b** (50% probability ellipsoids; arbitrary numbering of the atoms; solvent molecules omitted)

corresponding selenosemicarbazides **5** and **7**, respectively. It is worth mentioning that, in the case of **1**, the *N*-oxide function is preserved. Upon heating in DMF at 100° in the presence of air O_2, **7b** undergoes a cyclization to give 1,3,4-oxadiazole **8a**, whereas compounds **5** decompose under these conditions. The same product **8a** is formed from **6b** and **4a** in DMF under air atmosphere at 100°. In contrast to thiosemicarbazides [7a], the Se analogs **7** undergo cyclization to give 1,2,4-triazole-3-selones **9** under mild thermal conditions, and no catalyst is required. To the best of our knowledge, this is the first type of cyclization of selenosemicarbazides, which occurs without loss of Se.

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Experimental Part

1. *General.* M.p.: *Melt-Temp. II* (*Aldrich*) or *STUART SMP30*; uncorrected. IR Spectra: *NEXUS FT-IR* spectrophotometer; in KBr; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker Avance III* (600 and 150 MHz, resp.), using solvent signal as reference; δ in ppm; J in Hz; assignments of signals in ^{13}C-NMR spectra accomplished by HMQC experiments. HR-ESI-MS: *Bruker maXis* spectrometer; in *m*/*z*.

2. *Starting Materials.* All solvents are commercially available and were used as received. Carbohydrazides **1a** and **1b** were prepared from the corresponding esters by treatment with $NH_2NH_2 \cdot H_2O$ as described in [7b].

3. *Synthesis of Selenosemicarbazides* **5a**–**5d** *and* **7a**–**7g**. *General Procedure.* A mixture of **1** or **6** (1 mmol), and the corresponding isoselenocyanate **4** (1.1 mmol) in MeOH (5 ml) was stirred for 48 h. Then, the product formed was filtered off, washed with MeOH, and crystallized from an acetone/MeOH mixture (1:1).

*2-[(1,5-Dimethyl-3-oxido-1*H*-imidazol-4-yl)carbonyl]-*N*-(4-fluorophenyl)hydrazinecarboselenoamide* (**5a**). Yield: 0.326 g (88%). Colorless crystals. M.p. 198–200° (MeOH). IR (KBr): 3154*s* (NH), 3054*m*, 2934*m*, 1671v*s* (C=O), 1636v*s*, 1597*s*, 1510*s*, 1463*s*, 1227*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.13 (br. *s*, NH); 8.48 (*s*, H–C(2)); 7.41–7.13 (*m*, 4 arom. H); 3.59 (*s*, MeN); 2.49 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 179.4 (C=O); 159.9 (C=Se); 149.5, 137.8, 132.0, 120.5 (2 arom. C, C(4,5)); 129.2, 115.0 (4 arom. CH); 126.9 (C(2)); 32.4 (MeN); 9.5 (*Me*–C(5)). HR-ESI-MS: 372.0367 ($[M+H]^+$, $C_{13}H_{15}FN_5O_2Se^+$; calc. 372.0370).

*2-[(1,5-Dimethyl-3-oxido-1*H*-imidazol-4-yl)carbonyl]-*N*-(4-methoxyphenyl)hydrazinecarboselenoamide* (**5b**). Yield: 0.272 g (71%). Colorless crystals. M.p. 175–176° (MeOH). IR (KBr): 3157*s* (NH), 2933*m*, 1671v*s* (C=O), 1637v*s*, 1601*s*, 1512*s*, 1459*s*, 1255*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.02 (br. *s*, NH); 8.48 (*s*, H–C(2)); 7.27, 6.88 (*AA′BB′*, J_{AB} = 7.6, 4 arom. H); 3.75 (*s*, MeO); 3.59 (*s*, MeN); 2.49 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 179.7 (C=O); 159.9 (C=Se); 155.0, 137.4, 131.8, 119.1 (2 arom. C, C(4,5)); 128.4, 114.8 (4 arom. CH); 126.8 (C(2)); 55.7 (MeO); 32.4 (MeN); 9.5 (*Me*–C(5)). HR-ESI-MS: 384.0567 ([M + H]$^+$, $C_{14}H_{18}N_5O_3Se^+$; calc. 384.0570).

*2-[(1-Benzyl-5-methyl-3-oxido-1*H*-imidazol-4-yl)carbonyl]-*N*-(4-fluorophenyl)hydrazinecarboselenoamide* (**5c**). Yield: 0.381 g (85%). Colorless crystals. M.p. 180–181° (MeOH). IR (KBr): 3127*s* (NH), 3061*m*, 1667v*s* (C=O), 1598*s*, 1508*s*, 1481*s*, 1215*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.17, 10.10 (2br. *s*, NH); 8.74 (*s*, H–C(2)); 7.43–7.13 (*m*, 9 arom. H); 5.26 (*s*, CH$_2$); 2.45 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 180.0 (C=O); 164.7 (C=Se); 143.5, 139.9, 135.8, 131.4, 119.3 (3 arom. C, C(4,5)); 126.8 (C(2)); 129.5, 128.7, 127.8, 127.1, 116.2 (9 arom. CH); 48.8 (CH$_2$); 9.8 (Me). HR-ESI-MS: 448.0681 ([M + H]$^+$, $C_{19}H_{19}FN_5O_2Se^+$; calc. 448.0683).

*2-[(1-Benzyl-5-methyl-3-oxido-1*H*-imidazol-4-yl)carbonyl]-*N*-phenylhydrazinecarboselenoamide* (**5d**). Yield: 0.270 g (63%). Colorless crystals. M.p. 192–193° (MeOH). IR (KBr): 3216*m*, 3127*s* (NH), 3044*m*, 1667v*s* (C=O), 1597*s*, 1479*s*, 1328*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.13 (br. *s*, NH); 8.72 (*s*, H–C(2)); 7.41–7.17 (*m*, 10 arom. H); 5.26 (*s*, CH$_2$); 2.45 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 179.6 (C=O); 159.8 (C=Se); 139.9, 135.8, 131.4, 121.9 (2 arom. C, C(4,5)); 126.8 (C(2)); 129.5, 128.7, 128.6, 127.7, 127.6, 126.3 (10 arom. CH); 48.8 (CH$_2$); 9.8 (Me). HR-ESI-MS: 430.0774 ([M + H]$^+$, $C_{19}H_{20}N_5O_2Se^+$; calc. 430.0777).

N-*(4-Methoxyphenyl)-2-{[(1,4,5-trimethyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}hydrazinecarboselenoamide* (**7a**). Yield: 0.246 g (58%). Colorless crystals. M.p. 132–134° (MeOH). IR (KBr): 3273*m*, 3124*m* (NH), 2943*m*, 1692*s* (C=O), 1540*s*, 1512v*s*, 1246*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.31 (br. *s*, NH); 9.98 (br. *s*, NH); 7.21, 6.88 (*AA′BB′*, J_{AB} = 7.6, 4 arom. H); 3.75 (*s*, MeO); 3.52 (*s*, CH$_2$); 3.48 (*s*, MeN); 2.04, 1.67 (2*s*, 2 Me). ^{13}C-NMR ((D$_6$)DMSO): 179.8 (C=O); 164.8 (C=Se); 157.8, 136.3, 133.7, 126.3, 119.1 (2 arom. C, C(2,4,5)); 128.8, 114.8 (4 arom. CH); 55.7 (MeO); 36.8 (CH$_2$); 31.5 (MeN); 12.4, 9.2 (2 Me). HR-ESI-MS: 428.0654 ([M + H]$^+$, $C_{16}H_{22}N_5O_2SSe^+$; calc. 428.0654).

N-*(4-Fluorophenyl)-2-{[(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}hydrazinecarboselenoamide* (**7b**). Yield: 0.323 g (60%). Colorless crystals. M.p. 143–144° (MeOH). IR (KBr): 3289*s*, 3214*s* (NH), 2976*m*, 1686*s* (C=O), 1530v*s*, 1506v*s*, 1208*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.48 (br. *s*, NH); 10.19 (br. *s*, NH); 9.95 (br. *s*, NH); 7.34–7.07 (*m*, 14 arom. H); 3.95 (*s*, CH$_2$); 3.40 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO): 167.8 (C=O); 160.7 (C=Se); 157.6, 141.1, 137.8, 131.4, 126.5, 119.1 (4 arom. C, C(2,4,5)); 131.0, 130.7, 129.6, 129.4, 129.2, 128.5, 126.5, 115.1 (14 arom. CH); 36.0 (CH$_2$); 32.2 (MeN). HR-ESI-MS: 540.0763 ([M + H]$^+$, $C_{25}H_{23}FN_5OSSe^+$; calc. 540.0768).

N-*(4-Methoxyphenyl)-2-{[(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}hydrazinecarboselenoamide* (**7c**). Yield: 0.336 g (61%). Colorless crystals. M.p. 175–176° (MeOH). IR (KBr): 3370*s*, 3208*s* (NH), 2953*m*, 1690*s* (C=O), 1541v*s*, 1510*s*, 1244*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.47 (br. *s*, NH); 10.07 (br. *s*, NH); 9.87 (br. *s*, NH); 7.52–6.82 (*m*, 14 arom. H); 3.94 (*s*, CH$_2$); 3.74 (*s*, MeO); 3.40 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO): 165.3 (C=O); 162.6 (C=Se); 157.7, 141.7, 137.7, 131.4, 126.5, 113.6 (4 arom. C, C(2,4,5)); 134.5, 131.0, 130.6, 129.6, 129.4, 128.5, 128.4, 126.8 (14 arom. CH); 55.7 (MeO); 36.1 (CH$_2$); 32.2 (MeN). HR-ESI-MS: 552.0965 ([M + H]$^+$, $C_{26}H_{26}N_5O_2SSe^+$; calc. 552.0968).

*2-{[(1,5-Dimethyl-4-phenyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}-*N*-(4-methoxyphenyl)hydrazinecarboselenoamide* (**7d**). Yield: 0.312 g (64%). Colorless crystals. M.p. 169–171° (MeOH). IR (KBr): 3301*s*, 3154*s* (NH), 2947*m*, 1697v*s* (C=O), 1530*s*, 1512*s*, 1245*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.36 (br. *s*, NH); 10.01 (br. *s*, NH); 9.90 (br. *s*, NH); 7.35–6.81 (*m*, 9 arom. H); 3.77 (*s*, CH$_2$); 3.73 (*s*, MeO); 3.57 (*s*, MeN); 2.33 (s, Me). ^{13}C-NMR ((D$_6$)DMSO): 179.7 (C=O); 167.9 (C=Se); 157.7, 138.9, 137.5, 135.2, 132.9, 126.5 (3 arom. C, C(2,4,5)); 128.7, 128.5, 127.2, 127.0, 113.6 (9 arom. CH); 55.7 (MeO); 36.6 (CH$_2$); 31.5 (MeN); 10.7 (Me). HR-ESI-MS: 490.0810 ([M + H]$^+$, $C_{21}H_{24}N_5O_2SSe^+$; calc. 490.0811).

*2-{[(1,5-Dimethyl-4-phenyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}-*N*-(4-fluorophenyl)hydrazinecarboselenoamide* (**7e**). Yield: 0.400 g (83%). Colorless crystals. M.p. 172–173° (MeOH). IR (KBr): 3256*s* (NH), 3055*m*, 1686v*s* (C=O), 1541*s*, 1508*s*, 1212*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.00 (br. *s*, NH); 7.50–6.65 (*m*, 9 arom. H); 3.70 (*s*, CH$_2$); 3.60 (*s*, MeN); 2.30 (*s*, Me).

*2-{[(1-Benzyl-4,5-dimethyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}-*N*-(4-fluorophenyl)hydrazinecarboselenoamide* (**7f**). Yield: 0.370 g (75%). Colorless crystals. M.p. 158–160° (MeOH). IR (KBr): 3330*m*, 3126*m* (NH), 3030*m*, 1698v*s* (C=O), 1552*s*, 1508*s*, 1215*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.65 (br. *s*, NH); 7.60–6.80 (*m*, 9 arom. H); 5.20 (*s*, PhCH_2); 3.45 (*s*, SCH_2); 2.00, 1.75 (2*s*, 2 Me).

*2-{[(1-Benzyl-4,5-dimethyl-1*H*-imidazol-2-yl)sulfanyl]acetyl}-*N*-(4-methoxyphenyl)hydrazinecarboselenoamide* (**7g**). Yield: 0.430 g (86%). Colorless crystals. M.p. 142–144° (MeOH). IR (KBr): 3165*m*, 3127*m* (NH), 2955*m*, 1696v*s* (C=O), 1510*s*, 1455*m*, 1243*m*. ^{1}H-NMR ((D$_6$)DMSO): 9.80 (br. *s*, NH); 8.30 (br. *s*, NH); 7.50–6.75 (*m*, 9 arom. H); 5.05 (*s*, PhCH_2); 3.75 (*s*, MeO); 3.50 (*s*, SCH_2); 1.95, 1.90 (2*s*, 2 Me).

4. *General Procedure for the Synthesis of Hydrazides* **6** [8]. To a soln. of a 1*H*-imidazole-2-thione (1 mmol) in CH_2Cl_2 (5 ml) was added methyl 2-bromoacetate (1 mmol). The mixture was stirred for 48 h at r.t., then, the solvent was evaporated *i.v.*, and the residue was used immediately without further purification. The oily residue was dissolved in EtOH (5 ml), and $NH_2NH_2 \cdot H_2O$ (2 mmol) was added. The mixture was heated at reflux for 4 h, the solvent was evaporated *i.v.*, and the residue was crystallized from MeOH.

*2-[(1,4,5-Trimethyl-1*H*-imidazol-2-yl)sulfanyl]acetohydrazide* (**6a**). Yield: 0.208 g (97%). Colorless crystals. M.p. 135–136° (MeOH). IR (KBr): 3336*m*, 3285*m* (NH), 2941*m*, 1683*s* (C=O), 1551*s*, 1436v*s*, 1229*m*. ^{1}H-NMR ((D$_6$)DMSO): 9.88 (br. *s*, NH); 3.59 (*s*, CH_2); 3.43 (*s*, MeN); 2.14, 2.11 (2*s*, 2 Me). ^{13}C-NMR ((D$_6$)DMSO): 170.3 (C=O); 138.1, 134.0, 125.3 (C(2,4,5)); 35.0 (CH_2); 30.8 (MeN); 12.7, 9.0 (2 Me). HR-ESI-MS: 215.0961 ([$M+H$]$^+$, $C_8H_{15}N_4OS^+$; calc. 215.0961).

*2-[(1-Methyl-4,5-diphenyl-1*H*-imidazol-2-yl)sulfanyl]acetohydrazide* (**6b**). Yield: 0.311 g (92%). Colorless oil. IR (KBr): 3316*m* (NH), 2944*m*, 1672v*s* (C=O), 1602*s*, 1503*s*, 1320*m*. ^{1}H-NMR ((D$_6$)DMSO): 9.99 (br. *s*, NH); 7.48–7.15 (*m*, 10 arom. H); 3.83 (*s*, CH_2); 3.37 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO): 170.2 (C=O); 142.1, 137.9, 133.6, 131.0, 126.4 (2 arom. C, C(2,4,5)); 130.7, 130.1, 129.2, 129.0, 128.3, 126.8 (10 arom. CH); 34.3 (CH_2); 31.6 (MeN). HR-ESI-MS: 339.1272 ([$M+H$]$^+$, $C_{18}H_{19}N_4OS^+$; calc. 339.1274).

*2-[(1,5-Dimethyl-4-phenyl-1*H*-imidazol-2-yl)sulfanyl]acetohydrazide* (**6c**). Yield: 0.207 g (75%). Colorless crystals. M.p. 112–113° (MeOH). IR (KBr): 3301*m*, 3218*m* (NH), 2980*m*, 1697v*s* (C=O), 1661*s*. ^{1}H-NMR ((D$_6$)DMSO): 9.33 (br. *s*, NH); 7.58–7.22 (*m*, 5 arom. H); 3.63 (*s*, CH_2); 3.54 (*s*, MeN); 2.36 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 167.6 (C=O); 138.8, 137.4, 135.5, 126.5 (1 arom. C, C(2,4,5)); 128.8, 127.2, 126.9 (5 arom. CH); 36.4 (CH_2); 31.4 (MeN); 10.9 (Me). HR-ESI-MS: 277.1118 ([$M+H$]$^+$, $C_{13}H_{17}N_4OS^+$; calc. 277.1118).

*2-[(1-Benzyl-4,5-dimethyl-1*H*-imidazol-2-yl)sulfanyl]acetohydrazide* (**6d**). Yield: 0.258 g (89%). Colorless crystals. M.p. 131–132° (MeOH). IR (KBr): 3321*m*, 3223*m* (NH), 2969*m*, 1671v*s* (C=O), 1542*s*, 1496*s*, 1421*m*. ^{1}H-NMR ($CDCl_3$): 9.90 (br. *s*, NH); 7.45–6.85 (*m*, 5 arom. H); 5.05 (*s*, PhCH_2); 3.80 (br. *s*, NH_2); 3.50 (*s*, SCH_2); 2.15, 2.00 (2*s*, 2 Me).

5. *Synthesis of* **8a**. *Procedure A*. A mixture of **6b** (1 mmol) and **4a** (1.1 mmol) in DMF (10 ml) was heated to 100° for 6 h under air atmosphere. The black Se powder was filtered off and washed with CH_2Cl_2 (10 ml). The combined filtrate was concentrated *i.v.*, and the residue was crystallized from acetone/MeOH 1:1.

Procedure B. Selenosemicarbazide **7b** (1 mmol) in DMF (10 ml) was heated to 100° for 6 h under air atmosphere, and the mixture was worked up as described in *Procedure A*.

*N-(4-Fluorophenyl)-5-{[(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)sulfanyl]methyl}-1,3,4-oxadiazol-2-amine* (**8a**). Yield: 0.330 g (72%; *Procedure A*); 0.321 g (70%; *Procedure B*). Colorless crystals. M.p. 123–124° (MeOH). IR (KBr): 3224*s* (NH), 2996*m*, 1504v*s*, 1238*m*. ^{1}H-NMR ((D$_6$)DMSO): 10.44 (br. *s*, NH); 7.57–7.10 (*m*, 14 arom. H); 4.51 (*s*, CH_2); 3.31 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO): 181.9, 160.7, 157.6, 138.5, 131.2, 126.5, 119.1 (oxadiazol C(2,5), 4 arom. C, imidazole C(2′,4′,5′)); 130.9, 129.7, 129.6, 129.4, 129.0, 128.5, 126.9, 116.0 (14 arom. CH); 36.3 (CH_2); 32.2 (MeN). HR-ESI-MS: 458.1448 ([$M+H$]$^+$, $C_{25}H_{21}FN_5OS^+$; calc. 458.1445).

6. *Synthesis of 1*H*-1,2,4-Triazole-5-selones* **9a**–**9d**. *Procedure A*. A mixture of **6** (1 mmol) and the corresponding isoselenocyanate **4** (1.1 mmol) in MeOH (10 ml) was heated at reflux for 4 h under N_2. Then, the product formed was filtered off, washed with MeOH, and crystallized from acetone/MeOH (1:1).

Procedure B. Selenosemicarbazide **7** (1 mmol) in MeOH (10 ml) was heated at reflux for 4 h under N_2. Then, the mixture was worked up as described in *Procedure A*.

*2,4-Dihydro-4-(4-methoxyphenyl)-5-{[(1,4,5-trimethyl-1*H*-imidazol-2-yl)sulfanyl]methyl}-3*H*-1,2,4-triazole-3-selone* (**9a**). Yield: 0.260 g (64%; *Procedure A*). Colorless crystals. M.p. 190–191° (MeOH). IR (KBr): 3006*m*, 2917*m*, 2881*m*, 1515*s*, 1465*s*, 1251*m*, 1171*m*. ^{1}H-NMR ((D$_6$)DMSO): 7.45–6.70 (*m*, 4 arom. H); 3.95 (*s*, CH_2); 3.85 (*s*, MeO); 3.30 (*s*, MeN); 2.05 (*s*, 2 Me). ESI-MS: 410 ($[M+H]^+$), 432 ($[M+Na]^+$), 448 ($[M+K]^+$).

*2,4-Dihydro-4-(4-methoxyphenyl)-5-{[(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)sulfanyl]methyl}-3*H*-1,2,4-triazole-3-selone* (**9b**). Yield: 0.301 g (57%; *Procedure A*); 0.317 g (60%; *Procedure B*). Colorless crystals. M.p. 133–135° (MeOH). IR (KBr): 3057*m*, 2928*m*, 1515*s*, 1454*s*, 1253*m*. ^{1}H-NMR ((D$_6$)DMSO): 14.20 (br. *s*, NH); 7.65–6.80 (*m*, 14 arom. H); 4.25 (*s*, CH_2); 3.75 (*s*, MeO); 3.30 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO): 160.3 (C=Se); 157.8, 155.6, 150.1, 134.7, 131.4, 131.0, 130.9, 126.5 (triazol C(2), 4 arom. C, imidazol C(2′,4′,5′)); 129.6, 129.3, 128.5, 126.8, 126.6, 124.4, 119.1, 114.8 (14 arom. CH); 55.5 (MeO); 49.1 (MeN); 32.2 (CH_2). HR-ESI-MS: 534.0859 ($[M+H]^+$, $C_{26}H_{24}N_5OSSe^+$; calc. 534.0862).

*5-{[(1-Benzyl-4,5-dimethyl-1*H*-imidazol-2-yl)sulfanyl]methyl}-2,4-dihydro-4-(4-methoxyphenyl)-3*H*-1,2,4-triazole-3-selone* (**9c**). Yield: 0.410 g (86%; *Procedure B*). Colorless crystals. M.p. 164–167° (MeOH). IR (KBr): 3066*m*, 2923*m*, 2857*m*, 1514*s*, 1254*m*, 1180*m*. ^{1}H-NMR ($CDCl_3$): 11.10 (br. *s*, NH); 7.35–6.70 (*m*, 9 arom. H); 5.05 (*s*, PhCH_2); 3.80 (*s*, MeO); 3.75 (*s*, SCH_2); 2.25, 1.95 (2*s*, 2 Me).

*4-(4-Fluorophenyl)-2,4-dihydro-5-{[(1,4,5-trimethyl-1*H*-imidazol-2-yl)sulfanyl]methyl}-3*H*-1,2,4-triazole-3-selone* (**9d**). Yield: 0.104 g (25%; *Procedure A*). Colorless crystals. M.p. 154–155° (MeOH). IR (KBr): 3181*m* (NH), 3033*m*, 2893*m*, 1540*s*, 1508v*s*, 1227*m*. ^{1}H-NMR ((D$_6$)DMSO): 14.34 (br. *s*, NH); 7.45–7.38 (*m*, 4 arom. H); 4.02 (*s*, CH_2); 3.28 (*s*, MeN); 2.04, 1.97 (2*s*, 2 Me). ^{13}C-NMR ((D$_6$)DMSO): 163.6 (C=Se); 161.9, 151.3, 134.3, 133.9, 130.6, 126.7 (triazol C(2), 2 arom. C, imidazol C(2′,4′,5′)); 131.2, 116.6 (4 arom. CH); 31.1 (MeN); 28.9 (CH_2); 13.0, 9.3 (2 Me). HR-ESI-MS: 398.0349 ($[M+H]^+$, $C_{15}H_{17}FN_5SSe^+$; calc. 398.0348).

7. *X-Ray Crystal-Structure Determination of* **7a**, **7d**, *and* **9b** (*Table* and *Figs. 1* and *2*)[6]). All measurements were performed on a *Nonius KappaCCD* diffractometer [11] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules **7d** and **9b** are shown in *Figs. 1* and *2*, respectively. Data reduction was performed with HKL Denzo and Scalepack [12]. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections based on the multi-scan method [13] were applied. Equivalent reflections, other than *Friedel* pairs in **9b**, were merged. The structures were solved by direct methods using SIR92 [14], which revealed the positions of all non-H-atoms. In the case of **7a**, the asymmetric unit contains two symmetry-independent molecules **7a** and one disordered molecule of $CHCl_3$. The solvent molecule could not be modelled satisfactorily, so the SQUEEZE routine [15] of the program PLATON [16] was employed. This procedure, which allows the disordered solvent molecules to be omitted entirely from the subsequent refinement model, gave better refinement results, and there were no significant peaks of residual electron density to be found in the voids of the structure. The procedure leaves one cavity of 303 Å^3 per unit cell. The electron count in the disordered region was calculated to be 80 e per cavity. One molecule of $CHCl_3$ per cavity corresponded with the peaks of residual electron density observed prior to the application of the SQUEEZE procedure. This yields 58 e and this estimate was used in the subsequent calculation of the empirical formula, formula weight, density, linear absorption coefficient, and $F(000)$. In all cases, the non-H-atoms were refined anisotropically. In the case of **9b**, the poor quality of the crystal and the subsequent data meant that it was necessary to restrain atom C(15) to have pseudo-isotropic displacement parameters. For **7a** and **7d**, the H-atoms of the NH groups were placed in the positions indicated by a difference electron-density map, and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms and all H-atoms of **9b** were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a

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[6]) CCDC-911592–911594 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table. *Crystallographic Data for Compounds* **7a**, **7d**, *and* **9b**

	7a	**7d**	**9b**
Crystallized from	$CHCl_3$	acetone/EtOH	MeOH
Empirical formula	$C_{16}H_{21}N_5O_2SSe \cdot 0.5\ CHCl_3$	$C_{21}H_{23}N_5O_2SSe$	$C_{26}H_{23}N_5OSSe \cdot CH_3OH$
Formula weight [g mol^{-1}]	486.02	488.40	564.50
Crystal color, habit	colorless, prism	colorless, prism	colorless, plate
Crystal dimensions [mm]	$0.20 \times 0.25 \times 0.30$	$0.15 \times 0.17 \times 0.20$	$0.05 \times 0.12 \times 0.25$
Temp. [K]	160(1)	160(1)	160(1)
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
Z	4	2	4
Reflections for cell determination	61134	19838	49048
2θ Range for cell determination [°]	4–55	4–60	4–50
Unit cell parameters:			
a [Å]	10.3983(2)	9.5183(2)	8.174(1)
b [Å]	12.7273(2)	9.7896(2)	46.768(7)
c [Å]	15.9518(2)	12.7504(2)	6.943(1)
α [°]	84.0962(9)	95.948(1)	90
β [°]	88.1341(9)	98.419(1)	90
γ [°]	82.6491(7)	114.092(1)	90
V [Å^3]	2082.24(6)	1055.20(4)	2653.8(7)
D_x [g cm^{-3}]	1.550	1.537	1.413
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	2.117	1.906	1.526
Scan type	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{(\max)}$ [°]	55	60	50
Transmission factors (min; max)	0.610; 0.686	0.585; 0.756	0.625; 0.934
Total reflections measured	47740	30512	11242
Symmetry independent reflections	9492	6143	4008
Reflections with $I > 2\sigma(I)$	7535	5412	2548
Reflections used in refinement	9491	6143	4008
Parameters refined; restraints	485; 0	283; 0	329; 7
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0435	0.0617	0.0876
$wR(F^2)$ (all data)	0.1090	0.1739	0.2268
Weighting parameters [a; b][a])	0.0631; 0	0.1216; 0.7324	0.0825; 11.7070
Goodness of fit	1.070	1.075	1.152
Secondary extinction coefficient	0.0148(8)	–	0.027(2)
Final $\Delta_{\max}/\sigma$	0.003	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.63; −0.52	1.65; −0.74	1.02; −0.92

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$

fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom (1.5 U_{eq} for Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. In the cases of **7a** and **9b**, a correction for secondary extinction was applied, and one reflection of **7a**, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. For **9b**, refinement of the absolute structure parameter [17] yielded a value of −0.02(3), which confidently confirms that the refined model corresponds with the true absolute structure. Neutral atom-scattering factors for non-H-atoms were taken from [18a], and the scattering factors for H-atoms were taken from [19]. Anomalous dispersion effects were included in F_c [20]; the values for f' and f'' were those of [18b]. The values of the mass

attenuation coefficients are those of [18c]. All calculations were performed using the SHELXL97 [21] program.

REFERENCES

[1] a) M. Koketsu, H. Ishihara, *Curr. Org. Synth.* **2006**, *3*, 439; b) D. R. Garud, M. Koketsu, H. Ishihara, *Molecules* **2007**, *17*, 504; c) H. Heimgartner, Y. Zhou, P. K. Atanassov, G. L. Sommen, *Phosphorus, Sulfur Silicon* **2008**, *183*, 840; d) M. Ninomiya, D. R. Garud, M. Koketsu, *Heterocycles* **2010**, *81*, 2027.

[2] M. Ninomiya, D. R. Garud, M. Koketsu, *Coord. Chem. Rev.* **2011**, *255*, 2968; M. A. Crampsie, M. K. Pandey, D. Desai, J. Spallholz, S. Amin, *Chem. Biol. Interact.* **2012**, *200*, 28.

[3] Ó. López, S. Maza, V. Ulgar, I. Maya, J. G. Fernández-Bolaños, *Tetrahedron* **2009**, *65*, 2556.

[4] a) C. Collard-Charon, R. Huls, M. Renson, *Bull. Soc. Chim. Belg.* **1962**, *71*, 541; b) K. A. Jensen, G. Felbert, C. T. Pedersen, U. Svanholm, *Acta Chim. Scand.* **1966**, *20*, 278; c) E. Bulka, D. Ehlers, *J. Prakt. Chem. (Leipzig)* **1973**, *315*, 155; d) P. F. De Athayde-Filho, A. M. Simas, S. M. Cruz Gonçalves, J. Miller, *Phosphorus, Sulfur Silicon* **2000**, *161*, 115; e) M. Koketsu, Y. Yamamura, H. Ishihara, *Heterocycles* **2006**, *68*, 1191; f) Y. Xie, J. Liu, J. Li, *Tetrahedron Lett.* **2011**, *52*, 932.

[5] Y. Xie, J. Liu, P. Yang, X. Shi, J. Li, *Tetrahedron* **2011**, *67*, 5369.

[6] A. A. Hassan, A. M. Shawky, *J. Heterocycl. Chem.* **2010**, *47*, 745.

[7] a) A. M. Pieczonka, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **2012**, *95*, 404; b) G. Mlostoń, A. M. Pieczonka, E. Kowalczyk, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2011**, *94*, 1764.

[8] G. Mlostoń, T. Gendek, H. Heimgartner, *Helv. Chim. Acta* **1998**, *81*, 1585.

[9] C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.

[10] J. Bernstein, R. E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem., Int. Ed.* **1995**, *34*, 1555.

[11] R. Hooft, KappaCCD Collect Software, *Nonius BV*, Delft, The Netherlands, 1999.

[12] Z. Otwinowski, W. Minor, in 'Methods in Enzymology', Vol. 276, 'Macromolecular Crystallography', Part A, Eds. C. W. Carter Jr., R. M. Sweet, Academic Press, New York, 1997, p. 307.

[13] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

[14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[15] P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

[16] A. L. Spek, PLATON, Program for the Analysis of Molecular Geometry, University of Utrecht, The Netherlands, 2008.

[17] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908; H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.

[18] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 4.2.6.8, p. 219; c) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 4.2.4.3, p. 200.

[19] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.

[20] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.

[21] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

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