Selenium-Containing Heterocycles from Isoselenocyanates: Synthesis of 1,3-Selenazoles from *N*-Phenylimidoyl Isoselenocyanates

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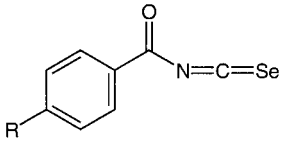
Dedicated to Prof. Dr. *Manfred Hesse* on the occasion of his 65th birthday

The reaction of *N*-phenylbenzamides **5** with excess $SOCl_2$ under reflux gave *N*-phenylbenzimidoyl chlorides **6**, which, on treatment with KSeCN in acetone, yielded imidoyl isoselenocyanates of type **2**. These products, obtained in almost quantitative yield, were stable in the crystalline state. They were transformed into selenourea derivatives **7** by the reaction with NH_3, or primary or secondary amines. In acetone at room temperature, **7** reacted with activated bromomethylene compounds such as 2-bromoacetates, acetamides, and acetonitriles, as well as phenacyl bromides and 4-cyanobenzyl bromide to to give 1,3-selenazol-2-amines of type **9** (*Scheme 2*). A reaction mechanism *via* alkylation of the Se-atom of **7**, followed by ring closure and elimination of aniline, is most likely (*cf. Scheme 7*). In the case of selenourea derivatives **7d** and **7l** with an unsubstituted NH_2 group, an alternative ring closure *via* elimination of H_2O led to 1,3-selenazoles **10a** and **10b**, respectively (*Schemes 4* and *7*). On treatment with NaOH, ethyl 1,3-selenazole-5-carboxylates **9l** and **9s** were saponified and decarboxylated to give the corresponding 5-unsubstituted 1,3-selenazoles **12a** and **12b** (*Scheme 6*). The molecular structures of selenourea **7f** and the 1,3-selenazoles **9c** and **9d** have been established by X-ray crystallography (*Figs. 1* and *3*).

1. Introduction. – With the aim of using less-toxic selenium compounds for the synthesis of selenaheterocycles, we have prepared arenecarbonyl isoselenocyanates **1** from KSeCN and arenecarbonyl chlorides as precursors [1]. These transient intermediates could not be isolated, because they readily oligomerized to give a mixture of oligomers. This is the reason for low yields of products from reactions with these intermediates, *e.g.*, the formation of selenourea derivatives [1][2]. In our previous paper, we have shown that the *in situ* generated arenecarbonyl isoselenocyanates **1** can be trapped by ethyl diazoacetate, leading to 1,2,3-selenadiazole derivatives *via* a 1,3-dipolar cycloaddition [1].



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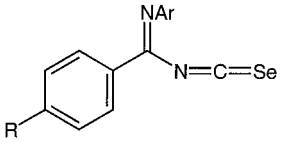

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Surprisingly, the relatively stable *N*-phenylimidoyl isoselenocyanates **2** (Ar = Ph), which can be conveniently prepared from *N*-phenylimidoyl chlorides and KSeCN, have been only rarely investigated. To the best of our knowledge, there is only one report on

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these heterocumulenes, which seem to be attractive synthons for Se-containing compounds. *Kirsanova* and *Derkach* described, *e.g.*, the reaction of **2** (Ar = Ph, R = H) with aniline in which the corresponding selenourea derivative was formed [3].

On the other hand, the synthesis of 1,3-selenazoles is still an attractive goal. The known syntheses rely mainly on the *Hantzsch* reaction [4] (*cf. Scheme 1*). They require selenoureas or selenoamides that, in turn, have to be prepared by treatment of cyanamides and nitriles, respectively, with H_2Se [5]. Compared with H_2S, H_2Se is more toxic and more difficult to handle [6]. But the search for alternative syntheses of 1,3-selenazoles was rarely successful, in contrast to those of analogous 1,3-thiazoles. For example, a convenient method for the preparation of 1,3-thiazoles from α-thiocyanatoacetophenones and primary amines, which does not involve H_2S [7], was shown to be unusable for the synthesis of 1,3-selenazoles [8]. In a recent re-investigation of these experiments, the formation of a series of acyclic arenecarbonylcarboselenoamides has been observed, but no 1,3-selenazole could be detected [9]. Some special 1,3-selenazoles, *e.g.*, those unsubstituted at C(2), are accessible in moderate yield by the reaction between isocyanides with an acidic H-atom in α-position and isoselenocyanates [10]. Another useful starting material for the preparation of 1,3-selenazoles proved to be allenyl isoselenocyanate, which was obtained from propynyl selenocyanate by a [3.3]-sigmatropic rearrangement [11].

The synthesis of selenoureas and selenoamides, which are both potential precursors of 1,3-selenazoles, has been investigated by several groups with the aim of avoiding H_2Se. For example, *Hartmann* explored a synthesis of *N*,*N*-dialkylselenoamides by treating corresponding *S*-alkylated thioamides with Na_2Se, which was generated *in situ* from elemental Se and Na in DMF [12]. Analogously, tri- and tetrasubstituted thioureas were transformed into the corresponding selenoureas [13]. The overall reaction is a conversion of a C=S to a C=Se group. In a similar reaction, the transformation of a C=O into a C=S group was achieved by using chloroimidates, and Na_2Se [14] or chloroiminium salts[2]) and NaHSe [15]. A possibly rather general selenating reagent for the conversion of C=O into C=Se groups is phenylphosphonoselenoic dichloride [16]. The reagent was readily prepared by the reaction of dichlorophenylphosphine with an excess of powdered Se at 170–175° in an inert atmosphere. The main drawback of earlier protocols for the selenation of carbonyl groups with P_2Se_5 was the low yield of product [17]. *Lai* and *Reid* reacted arenecarbonitriles with NaHSe and obtained selenoamides in high yield [18], and *Ruan et al.* generated NaHSe for the same purpose *in situ* from Se and $NaBH_4$ [19].

A useful approach to selenoureas is the reaction of isoselenocyanates with amines [20]. As a rule, aryl and alkyl isoselenocyanates are more difficult to synthesize than arenecarbonyl analogues. Whereas the preparation of the former needs two or more reaction steps [21], the latter can be easily synthesized by the reaction of arenecarbonyl chlorides with KSeCN [22] (*cf.* [1]).

Although *N*-(arylcarbonyl)selenoureas are easily accessible, they have not been used to synthesize 1,3-selenazoles according to the traditional *Hantzsch* reaction, until *Liebscher* and *Hartmann* modified the procedure [23] (*Scheme 1*). In the classical

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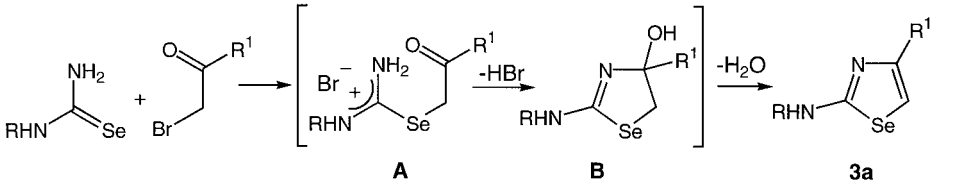
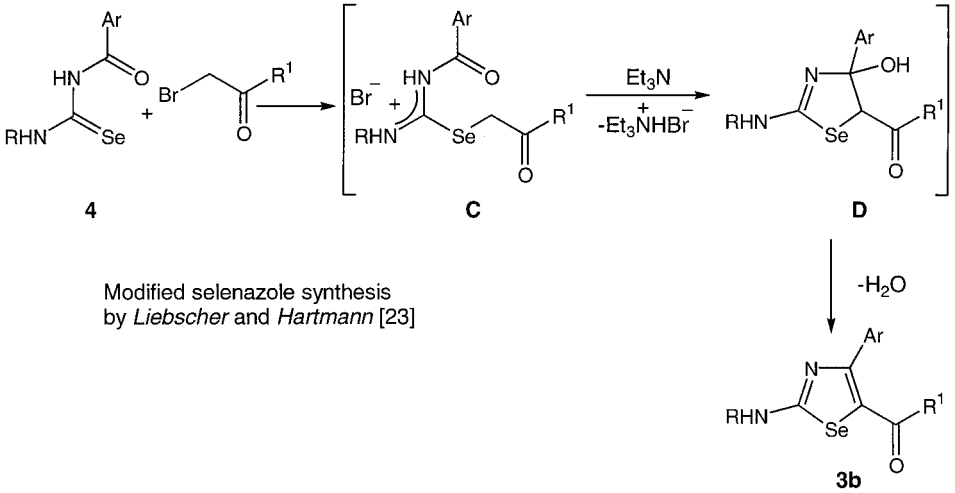
[2]) The chloroimidates and chloroiminium salts can be prepared conveniently by treatment of the corresponding amides with phosgene.

Hantzsch selenazole synthesis, the ring closure of the alkylated intermediate **A** occurs between the NH_2 group and the C=O group of the former α-bromocarbonyl compound to give **B**. On the other hand, the *N*-acylated intermediate **C**, on treatment with Et_3N, cyclizes *via* intramolecular nucleophilic attack of the activated CH_2 group onto the acyl C-atom to give **D**. Elimination of H_2O from **B** and **D** leads to the 1,3-selenazoles **3a** and **3b**, respectively. Later, this concept was extended to *N*-(phenylimidoyl)thioureas [24], *N*-(aminomethylene)thioureas [25], and *N*-(diaminomethylene)thioureas [26] for the synthesis of 1,3-thiazoles, to 2-aminovinyl selenoketones for preparing selenophenes and selenopyrones [27], and to *N*-(selenoacyl)carboximidamides (*N*-(selenoacyl)amidines) to synthesize 1,3-selenazoles [28]. In these cases, an amine molecule was eliminated after the cyclization step. However, in the preparation of *N*-(selenoacyl)-carboximidamide H_2Se is again needed as the source of Se. Based on the same concept, *N*,*N*-dimethyl-*N*′-[(dimethylamino)(selenocarbonyl)]formimidamide was also used as a starting material in the synthesis of 1,3-selenazoles [29]. The starting material itself was prepared by an elegant carbene reaction with elemental Se.

Scheme 1



Hantzsch's selenazole synthesis



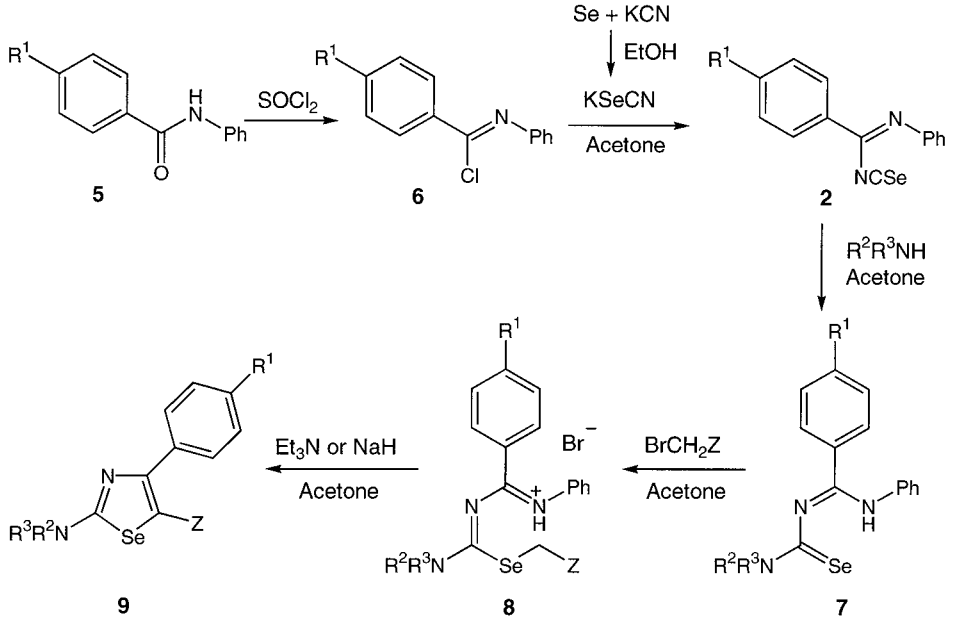
Modified selenazole synthesis by *Liebscher* and *Hartmann* [23]

In the present paper, we describe a new modification of the *Liebscher-Hartmann* synthesis [23] of 1,3-selenazoles from *N*-(*N*-phenylimidoyl)selenoureas, which leads to the products in high yield and purity. Unlike (arenecarbonyl)selenoureas **4**, which were

synthesized from transient arenecarbonyl isoselenocyanates **1** and amines in low yield (*cf.* [1]), (*N*-phenylimidoyl)selenoureas of type **7** (*cf. Scheme 2*) were prepared from stable *N*-phenylimidoyl isoselenocyanates **2**. The latter are easily accessible from *N*-phenylimidoyl chlorides **6** and KSeCN.

2. Results and Discussion. – A mixture of an *N*-phenylbenzamide of type **5** (*Scheme 2*) and 2–3 equiv. of $SOCl_2$ was heated to reflux until the evolution of SO_2 ceased. The excess $SOCl_2$ was evaporated, and the crude imidoyl chloride **6**, obtained as a white solid, was dried under vacuum for 24 h[3]). To this material, a freshly prepared solution of KSeCN[4]) in dry acetone was added, and the mixture was stirred at room temperature. After 30 min, the mixture was poured into ice-water, the precipitate was filtered and air-dried, and identified as imidoyl isoselenocyanate of type **2**. The yield was almost quantitative and the product was analytically pure without recrystallization. Compounds **2a**–**c** were rather stable at room temperature in the solid state but decomposed slowly in $CDCl_3$ and other organic solvents[5]). Nevertheless, it is recommended to store the products in the refrigerator.

Scheme 2



In the IR spectra (KBr) of **2a**–**c**, a strong absorption band at 1985–2053 cm^{-1} was characteristic for the isoselenocyanate structure as was the *singlet* at 138.9–140.1 ppm in the ^{13}C-NMR spectrum ($CDCl_3$). Furthermore, the compounds showed correct elemental analyses and intense peaks for $[M+1]^+$ (CI-MS) and $M^{+\cdot}$ (EI-MS).

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3) It is important to remove all $SOCl_2$ to achieve high yields of pure product in the following reaction.
4) KSeCN was prepared from elemental Se and KCN in EtOH solution and dried at *ca.* 120°.
5) In EtOH solution, Se precipitated on standing overnight at room temperature.

Table 1. *Yields of Isoselenocyanates* **2** *and Selenoureas* **7**

Compound	R^1	R^2	R^3	Yield [%]
2a	H	–		99
b	Me	–		99
c	Cl	–		98
7a	H	$-(CH_2)_2O(CH_2)_2-$		92
b	H	$-(CH_2)_4-$		74
c	H	$-(CH_2)_5-$		80
d	H	H	H	65
e	H	Me	Ph	84
f	Me	$-(CH_2)_2O(CH_2)_2-$		85
g	Me	H	H	60
h	Me	H	$PhCH_2$	95
i	Me	Me	Ph	85
j	Cl	$-(CH_2)_2O(CH_2)_2-$		82
k	Cl	Bu	Bu	97
l	Cl	H	H	75
m	Cl	Me	Ph	92

Treatment of solutions of **2a**–**c** in acetone with aqueous NH_3 (25%), primary or secondary amines at room temperature gave selenourea derivatives of type **7** in good-to-excellent yields (*Table 1*). In general, the reaction was fast, and after 5–30 min the starting material had disappeared (TLC). Whereas, with aliphatic amines, the reaction was smooth, yielding only one product, it was slower with *N*-methylaniline. In the latter case, the mixture showed several spots on TLC along with the main spot for **7**[6]). The lowest yields (60–75%) were obtained from the reactions with NH_3.

The structures of the selenourea derivatives of type **7** have been deduced from their spectral and analytical data, and, in the case of **7f**, the structure has been established by X-ray crystal-structure analysis (*Fig. 1*).

The crystal structure of **7f** shows that there is no conjugation between the π-systems of the molecule. Both phenyl rings, as well as the Se, C(1), N(5) plane, are twisted out of the plane formed by the atoms C(1), N(2), C(3), N(4), C(11), and C(18): this latter plane forms an angle of *ca.* 50° with that defined by Se, C(1), and N(5), and the torsion angles N(2)–C(3)–C(11)–C(16) and C(3)–N(4)–C(18)–C(19) are 35.7(4) and 35.8(4)°, respectively. The amidine H–N(4) forms an intermolecular H-bond with the Se-atom of a neighboring molecule. These interactions link the molecule into infinite one-dimensional chains that run parallel to the *z*-axis and have a graph set motif [31] of C(6).

In all cases in which the terminal urea N-atom of the selenourea bears one or two aliphatic substituents or is unsubstituted, there exists only one tautomer in $CDCl_3$ solution, as shown by NMR spectroscopy. On the other hand, two tautomers have been detected in the cases of **7e**, **7i**, and **7m**, *i.e.*, where a Me(Ph)N group is present. As the crystal structure of **7f** showed that the NH is the terminal group of the amidine structure, we expected that the same tautomer would be present in

[6]) Reactions with aniline were even more sluggish and led to complex mixtures and only low yields of the corresponding selenoureas.

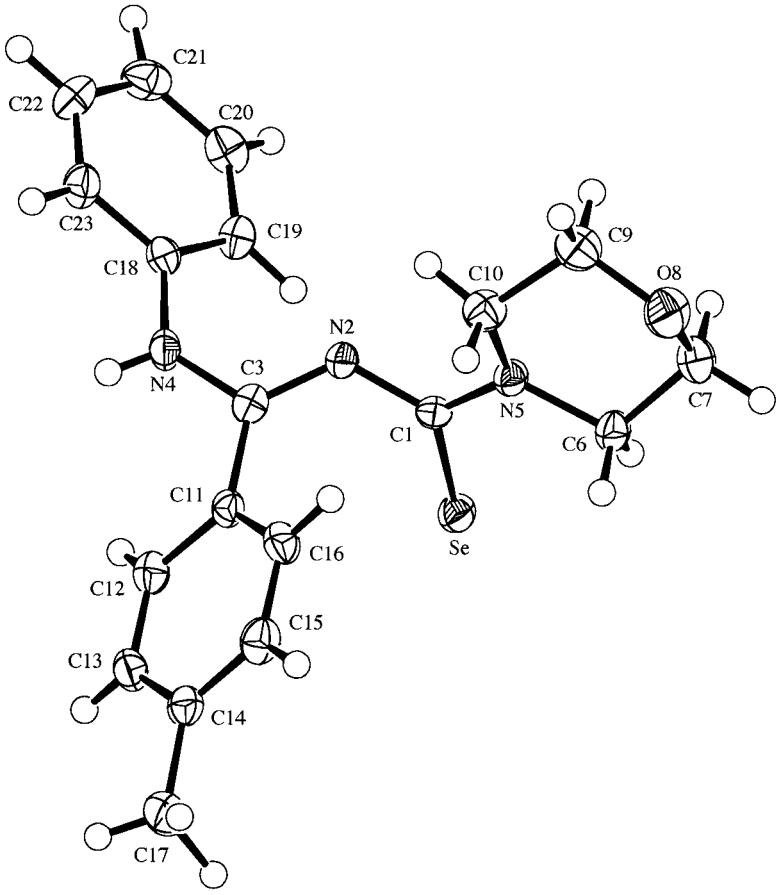


Fig. 1. *ORTEP Plot* [30] *of the molecular structure of* **7f** (with 50% probability ellipsoids; arbitrary numbering of the atoms)

$CDCl_3$ solution. Indeed, this was established by ^1H- and ^{13}C-COSY and HSQC and ^{15}N-HMBC experiments, from which the chemical shifts of all H-, C-, and N-atoms of **7f** could be assigned (*Fig. 2*,*a*). The position of the movable H-atom was determined by HMBC and ^{15}N-HMBC experiments, which correlated the H-atom (δ 11.5 ppm) of the NH group ($\delta(N) = -254$ ppm (*d*)) with the C-atoms at δ 132.1 (*s*) and 123.0 ppm (*d*), respectively, and the aromatic H-atom at δ 7.04 ppm with the N-atom of the NH group (^3J couplings). Therefore, the compounds **7** are N^2-[(amino)(selenocarbonyl)]-N^1-phenylarenecarboximidamides with a similar structure as some selenazadienes, which were used in hetero-*Diels-Alder* reactions (*cf.* [28][32]).

In the cases of selenoureas synthesized with *N*-methylaniline, *i.e.*, compounds **7e**, **7i**, and **7m**, two tautomers in a ratio of *ca.* 1:3 to 1:4 were present in $CDCl_3$ solution

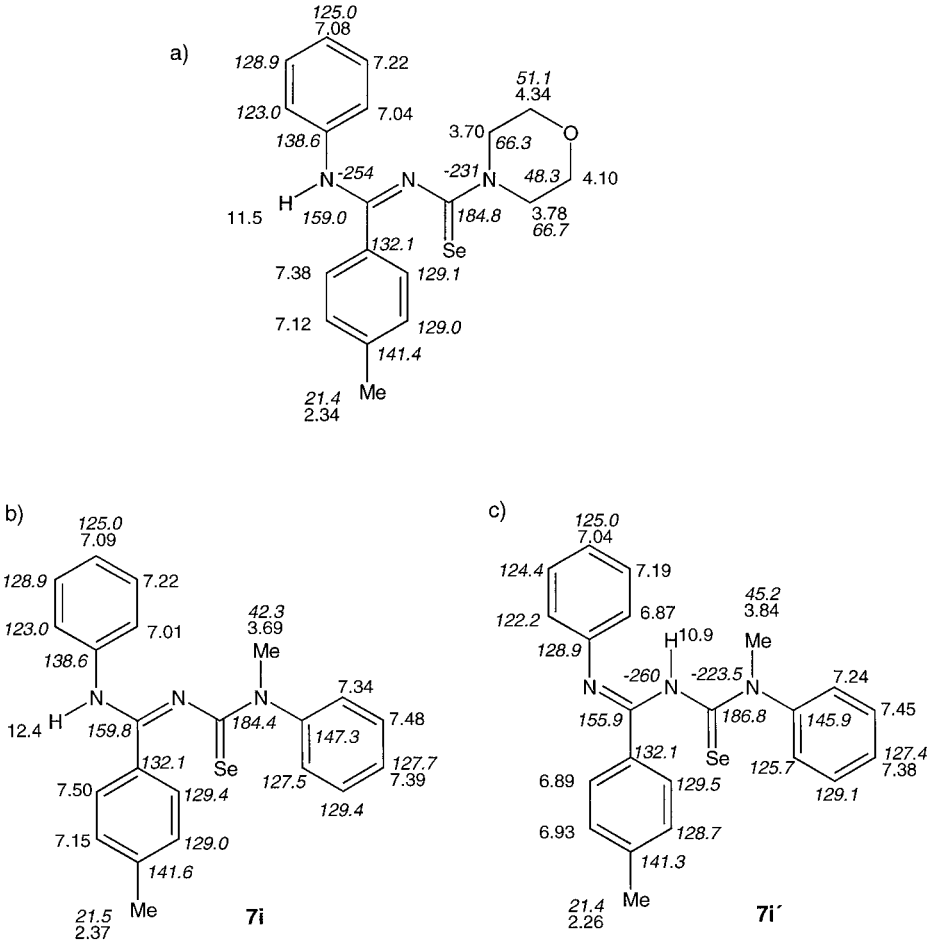


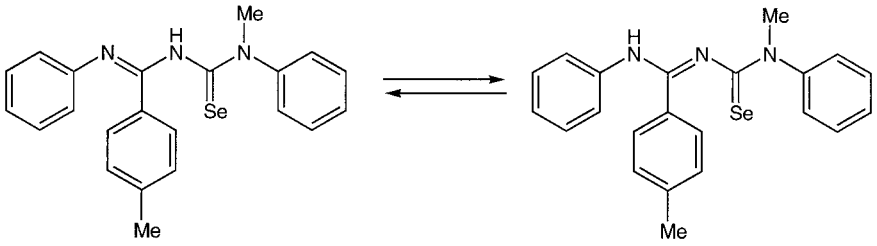
Fig. 2. *Assignment of chemical shifts of the H-, C-, and N-atoms of* a) **7f**, b) **7i**, *and* c) **7i′**

(NMR)[7]). For example, the ^{1}H-NMR spectrum of **7i** shows two signals for MeN (δ 3.84 and 3.69, ratio 3 : 1) and two for an aromatic Me group (δ 2.37 and 2.26 ppm, ratio 1 : 3) for the tautomers **7i** and **7i′** (*Scheme 3*). In **7i**, the C=Se group is conjugated with the 4-methylphenyl ring and, as a result of the electron-withdrawing effect, the chemical shift of the aromatic Me group is shifted to lower field compared with **7i′**. On the other hand, the signal of the MeN group of **7i** appears at higher field than in **7i′**, because the interaction of the N electron pair with C=Se is weakened by the conjugation of C=Se with the 4-methylphenyl ring. Based on this analysis, we propose that **7i′** is the major

[7]) We expected that one of the tautomers has a structure analogous to **7f**. Unfortunately, the correlation of NH with the C-atoms could not be observed in this case because of the rapid exchange between the tautomers. However, the ^{1}H-NMR spectrum allowed the decision which of the tautomers has the analogous structure to **7f**.

tautomer. The results of additional NMR studies supported this conclusion: by means of ^{1}H- and ^{13}C-COSY, HSQC, HMBC, and ^{15}N-HMBC experiments, the assignment of the H- and C-atoms of both tautomers **7i** and **7i′** was possible (*Fig. 2,b*). Based on the comparison of the spectra with those of **7f**, it was concluded that **7i** is the minor and **7i′** the major compound.

Scheme 3



7i′ (major) **7i** (minor)

In analogy to **7i**/**7i′**, we propose that, in **7e** and **7m**, the major tautomer is that in which C=Se is not conjugated with the benzamidine ring, *i.e.*, with the MeN signal at lower field (δ 3.81 (**7e′**) and 3.65 (**7e**); δ 3.82 (**7m′**) and 3.65 (**7m**)). In accordance with this assignment, the NH of the major tautomer absorbs at higher field (δ 10.8, 10.9, and 11.1 ppm for **7e′**, **7i′**, and **7m′**, resp., and δ 12.4, 12.4, and 12.7 ppm for **7e**, **7i**, and **7m**, resp.).

The *N,N*-disubstituted selenoureas of type **7**, *i.e.*, those with R^2, $R^3 \neq H$, reacted with α-bromoesters, amides, and nitriles, as well as with bromomethyl aryl ketones in acetone at room temperature to give the corresponding salts of type **8**. The reaction was complete after a few minutes. Even 4-(bromomethyl)benzonitrile reacted under the same conditions with **7i**/**7i′**. Treatment of the crude material with a small excess of Et_3N or NaH gave 1,3-selenazoles **9** *via* elimination of aniline as white or yellowish solids in high yields (*Scheme 2* and *Table 2*)[8]). According to NMR spectroscopy, the precipitated products were already pure, but, for characterization and elemental analysis, they were recrystallized from EtOH, Et_2O, or acetone.

The structures of 1,3-selenazoles **9a**–**t** were elucidated by means of their spectral data and elemental analyses, and, in the cases of **9c** and **9d**, they have been established by X-ray crystal-structure determination (*Fig. 3*). The two structures are very similar. In both cases, the 1,3-selenazole ring is planar, but none of the phenyl rings is coplanar with the five-membered ring.

The reaction of selenoureas with an NH_2 group, *e.g.*, **7d** and **7l**, with bromomethyl 4-nitrophenyl ketone in boiling acetone yielded a precipitate that we believe was a selenazolium salt. After trituration of the solid material with 5% aqueous NaOH solution, 1,3-selenazoles **10a** and **10b**, respectively, with unsubstituted C(5) were obtained (*Scheme 4*). The elemental analyses, as well as the mass spectra, showed that H_2O had been eliminated during cyclization, and the IR spectra indicated the absence

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[8]) The 1,3-selenazoles **9** can also be prepared by a one-pot reaction starting with isoselenocyanates **2** in acetone and successive addition of HNR^2R^3 and $BrCH_2Z$.

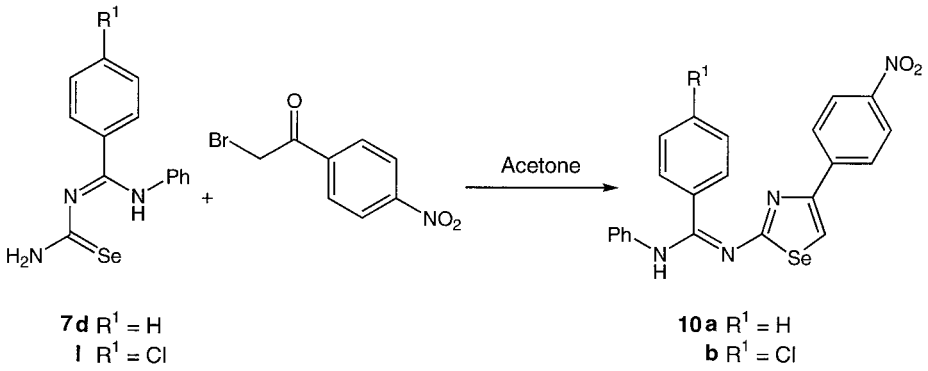
Table 2. *Yields of 1,3-Selenazoles* **9**

Compound	R^1	R^2	R^3	Z	Yield [%]
9a	H	$-(CH_2)_2O(CH_2)_2-$		4-$NO_2-C_6H_4CO$	90
b	H	$-(CH_2)_4-$		4-$NO_2-C_6H_4CO$	97
c	H	Me	Ph	4-$NO_2-C_6H_4CO$	95
d	H	$-(CH_2)_5-$		4-MeO$-C_6H_4CO$	98
e	H	$-(CH_2)_2O(CH_2)_2-$		EtOCO	88
f	H	$-(CH_2)_4-$		EtOCO	80
g	H	Me	Ph	EtOCO	79
h	H	Me	Ph	CN	85
i	Me	$-(CH_2)_2O(CH_2)_2-$		PhCO	96
j	Me	$-(CH_2)_2O(CH_2)_2-$		4-$NO_2-C_6H_4CO$	95
k	Me	$-(CH_2)_2O(CH_2)_2-$		H_2NCO	81
l	Me	$-(CH_2)_2O(CH_2)_2-$		EtOCO	85
m	Me	Me	Ph	CN	90
n	Me	Me	Ph	4-NC$-C_6H_4$	86
o	Cl	$-(CH_2)_2O(CH_2)_2-$		4-$NO_2-C_6H_4CO$	95
p	Cl	Bu	Bu	4-$NO_2-C_6H_4CO$	92
q	Cl	Me	Ph	4-$NO_2-C_6H_4CO$	99
r	Cl	Bu	Bu	EtOCO	94
s	Cl	Me	Ph	EtOCO	85
t	Cl	$-(CH_2)_2O(CH_2)_2-$		EtOCO	96
u	Cl	$-(CH_2)_2O(CH_2)_2-$		CN	95

of a C=O group. The NMR spectra showed that **10a** and **10b**, similarly as in the cases of **7e**, **7i**, and **7m**, each exist in $CDCl_3$ as a mixture of two tautomers in the ratio of *ca.* 5 : 1.

In most cases, treatment of the amidinium (= imidamidium) salts **8** (R^2,R^3 = H) with Et_3N led smoothly to 1,3-selenazoles **9**, but, in some experiments, the deprotonated intermediates **11** were isolated as stable products (*Scheme 5* and *Table 3*). These *N*-(imidoyl)isoselenourea derivatives were fully characterized. They were cyclized to give 1,3-selenazoles **9** by treatment with NaH in dry acetone. As an exception, **11f** could not be cyclized, probably because of the weak acidity of the CH_2 group.

Scheme 4



7d R^1 = H
l R^1 = Cl

10a R^1 = H
b R^1 = Cl

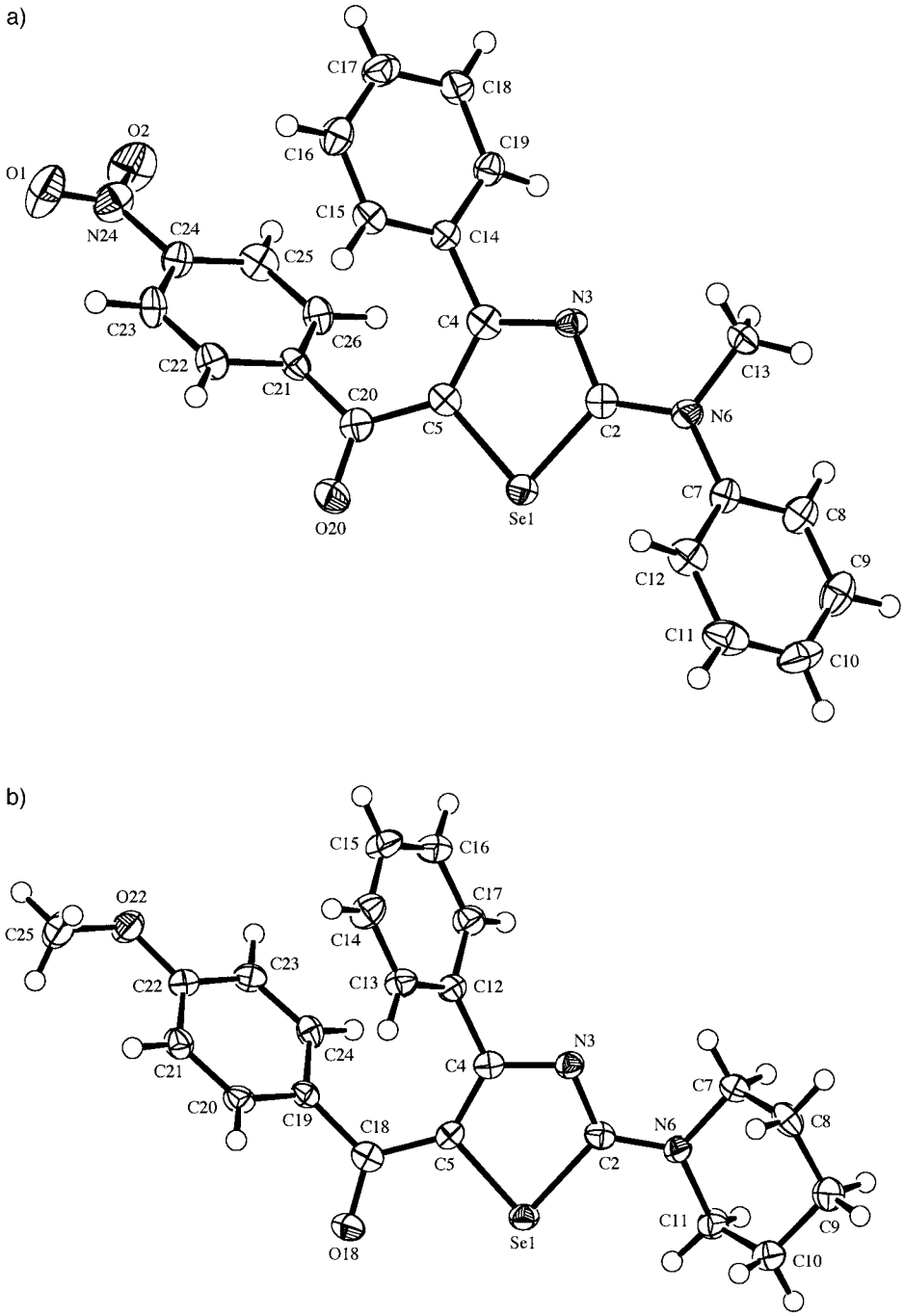


Fig. 3. *ORTEP Plots* [30] *of the molecular structure of* a) **9c** *and* b) **9d** (with 50% probability ellipsoids; arbitrary numbering of the atoms)

Scheme 5

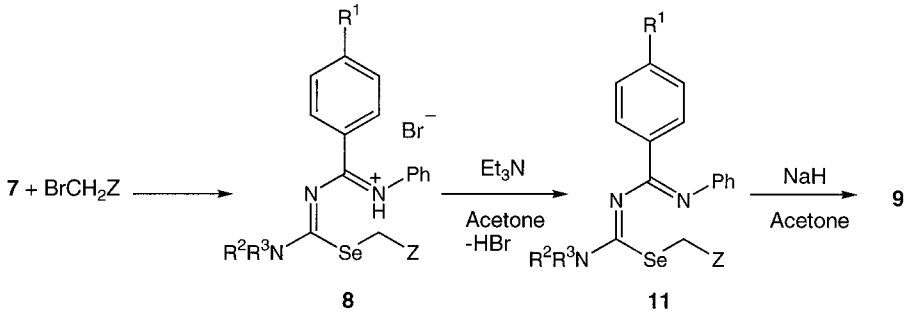
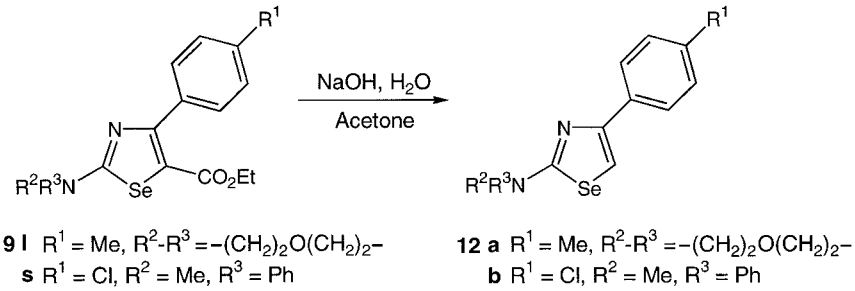


Table 3. *Yields of Isoselenoureas* **11**

Compound	R^1	R^2	R^3	Z	Yield [%]
11a	H	$-(CH_2)_2O(CH_2)_2-$		EtOCO	94
b	H	Me	Ph	CN	95
c	Me	Me	Ph	4-NC$-C_6H_4$	92
d	Me	$-(CH_2)_2O(CH_2)_2-$		4-NC$-C_6H_4$	94
e	Cl	$-(CH_2)_2O(CH_2)_2-$		EtOCO	87
f	Me	Me	Ph	NC$-CH_2$	85

Scheme 6



9 l R^1 = Me, R^2-R^3 = $-(CH_2)_2O(CH_2)_2-$
s R^1 = Cl, R^2 = Me, R^3 = Ph

12 a R^1 = Me, R^2-R^3 = $-(CH_2)_2O(CH_2)_2-$
b R^1 = Cl, R^2 = Me, R^3 = Ph

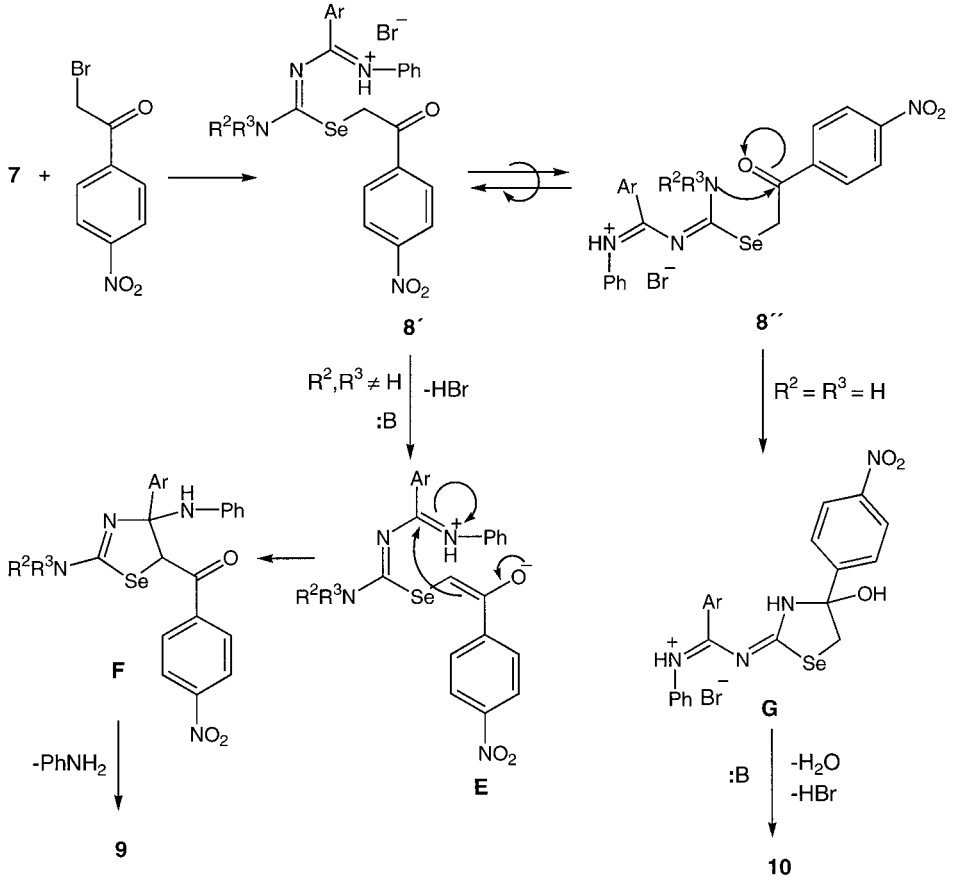
1,3-Selenazoles of type **9** with an EtOCO group at C(5), *e.g.*, **9l** and **9s**, after saponification with 5% NaOH solution under reflux, decarboxylated smoothly to give the corresponding 1,3-selenazoles **12a** and **12b**, respectively, with a free C(5) position (*Scheme 6*).

It is well-known that C(5) in 1,3-thiazoles possess a high electron density. Therefore, reactions with electrophiles such as aromatic diazonium salts, squaric acid, and *Vilsmeier* reagent [33] occur at C(5), yielding diazo dyes and other useful fine chemicals. In contrast, very few 1,3-selenazoles with a free C(5) position are known to date, and the reactivity of these compounds at the unsubstituted C(5) is still not clear. Though *Bulka* and *Ahlers* were successful in preparing diazo dyes from 2-(arylamino)-4-phenyl-1,3-selenazoles and aromatic diazonium salts [34] and *Keil* and *Hartmann* in their recent work prepared squarin dyes from 2,4-disubstituted 1,3-selenazoles [35], the chemical shifts of H$-$C(5) (selenazole moiety) of **12a** (7.29 ppm) and **12b** (7.18 ppm) indicate that the electron density is lower than in the analogous 1,3-thiazoles. For

example, H–C(5) (selenazole moiety) of 4-[4-(4-nitrophenyl)-1,3-thiazol-2-yl]morpholine absorbs at 6.94 ppm [7b] and that of 4-(4-phenyl-1,3-thiazol-2-yl)morpholine at 6.78 ppm [36].

The formations of 1,3-selenazoles **9** and **10**, respectively, *via* different ring-closure processes need a comment. Whereas compounds **9** were obtained from *N*,*N*-disubstituted selenourea derivatives (R^2, $R^3 \neq H$), 1,3-selenazoles **10** were the only observed products when *N*,*N*-unsubstituted **7** ($R^2 = R^3 = H$) were used in the reaction with activated bromomethylene compounds. In both cases, the first step of the reaction is the alkylation of the Se-atom leading to intermediate **8** (*Schemes 2* and *7*). With R^2, $R^3 \neq H$, the formation of the five-membered ring occurs *via* C-attack of the enolate onto the amidinium (imidamidium) group of **E** to give **F** (*Scheme 7*). Elimination of aniline then yields **9**. In the case of $R^2 = R^3 = H$, an alternative cyclization to a five-membered ring *via* nucleophilic attack of NH_2 in **8′** onto the C=O group leads to intermediate **G** and, after elimination of H_2O, to 1,3-selenazoles **10** (*Scheme 7*). The cyclization to **F** corresponds to that in the *Liebscher-Hartmann* synthesis whereas the ring closure to **G** proceeds as in the classical *Hantzsch* synthesis (*Scheme 1*).

Scheme 7



In conclusion, 4-aryl-1,3-selenazol-2-amines **9** with an electron-withdrawing group at C(5) are conveniently accessible *via* the reaction of selenourea derivatives of type **7** with activated bromomethylene compounds. The selenourea derivatives **7** are easily obtained from the reaction of benzimidoyl chlorides **6** and KSeCN, leading to benzimidoyl isoselenocyanates **2**, which on treatment with NH_3 or amines give **7**. As *N*-phenylbenzamides are the starting materials for the preparation of **6**, and KSeCN is smoothly prepared from elemental Se and KCN in EtOH, the described synthesis of 1,3-selenazoles **9** is cheap and safe as no highly toxic Se-compounds are used. A further advantage of the presented synthesis of 1,3-selenazole derivatives is the possibility of a one-pot reaction starting with *N*-phenylimidoyl isoselenocyanates **2**. The derivatives of type **9** were obtained in 80–95% yield.

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Experimental Part

1. *General*. See [1]. Atom numbering for the NMR data refer to the 1,3-selenazole moiety.

2. *Preparation of* N-*Phenylbenzimidoyl Isoselenocyanates* **2**: *General Procedure*. A mixture of a *N*-phenylbenzamide of type **5** and 2–3 equiv. $SOCl_2$ was heated to reflux for 2–3 h, until the evolution of SO_2 ceased. Excess $SOCl_2$ was evaporated, and the corresponding N-*phenylbenzimidoyl chloride* **6** was obtained as a white solid, which was dried *in vacuo* for 24 h. A freshly prepared soln. of KSeCN[9]) in acetone was added to **6** under stirring. Shortly after all of **6** had been dissolved, the yellowish benzimidoyl isoselenocyanate **2** crystallized from the soln. (in case of R^1 = Me or Cl). The mixture was poured on ice/H_2O under stirring, and the product was filtered by suction and air-dried.

N-*Phenylbenzimidoyl Isoselenocyanate* (**2a**). From 100.5 mmol of *N*-phenylbenzamide: 28.4 g (99%). Yellowish crystals. M.p. 59–60° (H_2O). IR: 3054*w*, 2105*m*, 2079*s*, 2053*s*, 1610*s*, 1589*m*, 1575*m*, 1481*m*, 1446*m*, 1311*w*, 1265*m*, 1206*m*, 1176*m*, 1072*w*, 1050*m*, 1022*m*. ^{1}H-NMR: 8.09 (*d*-like, 2 arom. H); 7.58–7.38 (*m*, 5 arom. H); 7.25 (*t*-like, 1 arom. H); 7.03 (*d*-like, 2 arom. H). ^{13}C-NMR: 148.0, 140.1 (2*s*, 2 arom. C); 139.3 (*s*, NCSe); 132.5 (*s*, CN_2); 132.3, 129.0, 128.7, 128.2, 125.6, 121.0 (6*d*, 10 arom. C). CI-MS: 287 ($[M+1]^+$). Anal. calc. for $C_{14}H_{10}N_2Se$ (285.21): C 58.95, H 3.51, N 9.82; found: C 58.80, H 3.55, N 9.81.

4-Methyl-N-*phenylbenzimidoyl Isoselenocyanate* (**2b**). From 162.5 mmol of 4-methyl-*N*-phenylbenzamide: 48.0 g (99%). Yellowish crystals. M.p. 103–103.5° (acetone). IR: 3053*w*, 2919*w*, 2092*m*, 1991*s*, 1657*w*, 1610*s*, 1591*s*, 1571*m*, 1508*m*, 1278*s*, 1202*s*, 1179*s*, 1170*m*, 1114*w*, 1074*w*, 1047*s*, 1016*m*. ^{1}H-NMR: 7.96 (*AA′* of *AA′BB′*, J = 8.3, 2 arom. H); 7.39 (*t*-like, 2 arom. H); 7.29–7.19 (*m*, 3 arom. H); 7.02 (*d*-like, 2 arom. H); 2.42 (*s*, Me). ^{13}C-NMR: 148.1, 143.0, 140.1 (3*s*, 3 arom. C); 138.9 (*s*, NCSe); 129.8 (*s*, CN_2); 129.4, 129.0, 128.1, 125.4, 121.0 (5*d*, 9 arom. C); 21.5 (*q*, Me). CI-MS: 301 ($[M+1]^+$). Anal. calc. for $C_{15}H_{12}N_2Se$ (299.24): C 60.20, H 4.01, N 9.36; found: C 60.13, H 4.06, N 9.36.

4-Chloro-N-*phenylbenzimidoyl Isoselenocyanate* (**2c**). From 100.7 mmol of 4-chloro-*N*-phenylbenzamide: 31.5 g (98%). Yellowish crystals. M.p. 92–92.5° (Et_2O). IR: 3064*w*, 2102*w*, 1986*s*, 1654*w*, 1610*s*, 1591*s*, 1568*m*, 1486*m*, 1448*m*, 1401*m*, 1300*w*, 1278*s*, 1206*s*, 1172*m*, 1106*w*, 1090*s*, 1072*m*, 1051*m*, 1012*m*. ^{1}H-NMR: 8.02 (*AA′* of *AA′BB′*, J = 8.0, 2 arom. H); 7.48–7.32 (*m*, 4 arom. H); 7.28–7.22 (*m*, 1 arom. H); 7.02 (*d*-like, 2 arom. H). ^{13}C-NMR: 147.8 (*s*, 1 arom. C); 140.1 (*s*, NCSe); 139.3, 138.6 (2*s*, 2 arom. C); 131.0 (*s*, CN_2); 129.4, 129.05, 128.98, 125.7, 121.0 (5*d*, 9 arom. C). EI-MS: 320 (0.5, $M^{+\bullet}$), 239 (2), 216 (20), 215 (10), 214 (82), 77 (100). Anal. calc. for $C_{14}H_9ClN_2Se$ (319.65): C 52.58, H 2.82, Cl 11.11, N 8.76; found: C 52.51, H 2.79, Cl 11.15, N 8.77.

3. *Preparation of Selenourea Derivatives* **7**: *General Procedure*. To a stirred soln. of **2** in acetone, 1 equiv. of NH_3, a primary or secondary amine was added at r.t. The soln. became orange immediately. After 5–30 min, **2** was completely consumed (TLC), and the soln. was poured into H_2O. In most of the cases, a yellow precipitate was formed during stirring for 1 h. When an emulsion was formed, the mixture was stirred for another few hours,

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[9]) The KSeCN used was prepared by dissolving powdered Se in a refluxing EtOH soln. of 1 equiv. of KCN. After stirring for 5 h, no Se was left, the EtOH was evaporated, and KSeCN was dried at 120° for 12 h.

and a small amount of $MgSO_4$ was added to accelerate the precipitation. The solid was filtered by suction and air-dried; the products were pure enough for further reaction. For anal. purposes, an aliquot was recrystallized to give yellow or yellowish crystals.

N^2-*[(Morpholin-4-yl)(selenocarbonyl)]*-N^1-*phenylbenzimidamide* (**7a**). From 10.2 mmol of **2a** and morpholine: 3.50 g (92%). M.p. 85–86° (dec., AcOEt). IR: 3444*w* (br.), 3178*m*, 3114*m*, 3046*m*, 2958*m*, 2894*m*, 2864*m*, 1608*s*, 1588*s*, 1574*s*, 1532*s*, 1481*s*, 1434*s*, 1358*m*, 1325*m*, 1312*s*, 1277*s*, 1223*s*, 1176*m*, 1154*w*, 1120*s*, 1112*s*, 1083*s*, 1025*m*. ^{1}H-NMR: 11.70 (*s*, NH); 7.60–6.95 (*m*, 10 arom. H); 4.37, 4.14 (2*t*, *J* = 4.9, 2 CH_2O); 3.81, 3.72 (2*t*, *J* = 4.9, 2 CH_2N). ^{13}C-NMR: 184.6, 159.1 (2*s*, CSe, CN_2); 138.3, 135.0 (2*s*, 2 arom. C); 130.8, 129.1, 128.9, 128.3, 125.1, 123.0 (6*d*, 10 arom. C); 66.7, 66.3 (2*t*, 2 CH_2O); 50.9, 48.3 (2*t*, 2 CH_2N). CI-MS: 374 (56, $[M+1]^+$), 294 (100). Anal. calc. for $C_{18}H_{19}N_3OSe$ (372.33): C 58.06, H 5.11, N 11.29; found: C 58.81, H 5.17, N 11.20.

N^1-*Phenyl*-N^2-*[(pyrrolidin-1-yl)(selenocarbonyl)]benzimidamide* (**7b**). From 3.8 mmol of **2a** and pyrrolidine: 1.00 g (74%). M.p. 145.5–146.5° (EtOH). IR: 3441*w* (br.), 3172*m*, 3109*m*, 3027*m*, 2962*m*, 2868*m*, 1616*s*, 1590*s*, 1576*s*, 1532*s*, 1490*s*, 1472*s*, 1439*s*, 1331*s*, 1282*m*, 1258*m*, 1223*m*, 1176*m*, 1110*w*, 1075*m*, 1027*w*, 1000*w*. ^{1}H-NMR: 12.00 (*s*, NH); 7.55–6.90 (*m*, 10 arom. H); 3.87, 3.80 (2*t*, *J* = 6.5, 2 CH_2N); 2.09–1.94 (*m*, 2 CH_2). ^{13}C-NMR: 180.3, 158.4 (2*s*, CSe, CN_2); 138.7, 135.3 (2*s*, 2 arom. C); 130.8, 129.4, 128.9, 128.2, 124.8, 123.0 (6*d*, 10 arom. C); 53.5, 50.7 (2*t*, 2 CH_2N); 25.6, 24.5 (2*t*, 2 CH_2). CI-MS: 358 (25, $[M+1]^+$), 278 (100). Anal. calc. for $C_{18}H_{19}N_3Se$ (356.33): C 60.67, H 5.34, N 11.80; found: C 60.55, H 5.51, N 11.75.

N^1-*Phenyl*-N^2-*[(piperidin-1-yl)(selenocarbonyl)]benzimidamide* (**7c**). From 3.0 mmol of **2a** and piperidine: 0.89 g (80%). M.p. 143–144° (EtOH). IR: 3442*w* (br.), 3242*m*, 3183*m*, 3106*m*, 3040*m*, 2933*m*, 2858*m*, 1621*s*, 1590*s*, 1541*s*, 1493*s*, 1460*s*, 1439*s*, 1367*m*, 1346*m*, 1327*m*, 1308*m*, 1282*s*, 1262*s*, 1234*s*, 1192*s*, 1177*m*, 1131*s*, 1122*m*, 1077*m*, 1061*m*, 1025*m*, 1001*m*. ^{1}H-NMR: 10.90 (*s*, NH); 7.53–6.97 (*m*, 10 arom. H); 4.28 (br. *s*, CH_2N); 3.80 (*t*, *J* = 6.5, CH_2N); 2.09–1.94 (*m*, 2 CH_2). ^{13}C-NMR: 183.4, 157.0 (2*s*, CSe, CN_2); 138.7, 135.0 (2*s*, 2 arom. C); 130.7, 129.1, 128.8, 128.2, 124.5, 122.5 (6*d*, 10 arom. C); 52.4, 49.0 (2*t*, 2 CH_2N); 26.1, 25.7, 24.4 (3*t*, 3 CH_2). CI-MS: 372 (100, $[M+1]^+$), 292 (67). Anal. calc. for $C_{19}H_{21}N_3Se$ (370.36): C 61.62, H 5.68, N 11.35; found: C 61.59, H 5.79, N 11.31.

N^2-*[Amino(selenocarbonyl)]*-N^1-*phenylbenzimidamide* (**7d**). From 10.4 mmol of **2a** and NH_3: 2.06 g (65%). M.p. 183–184° (dec.; acetone). IR: 3430*w* (br.), 3242*s*, 3188*s*, 3080*s*, 3040*m*, 1646*s*, 1599*s*, 1578*m*, 1522*s*, 1488*s*, 1446*s*, 1313*m*, 1286*s*, 1267*s*, 1221*s*, 1117*s*, 1075*w*, 1034*m*. ^{1}H-NMR: 11.77, 8.45, 7.70 (3*s*, 3 NH); 7.50–6.95 (*m*, 8 arom. H); 6.69 (*d*-like, 2 arom. H). CI-MS: 304 (44, $[M+1]^+$), 224 (45), 197 (100). Anal. calc. for $C_{14}H_{13}N_3Se$ (302.24): C 55.63, H 4.30, N 13.91; found: C 55.46, H 4.36, N 13.98.

N^1-*[[(Methyl)(phenyl)amino](selenocarbonyl)]*-N^2-*phenylbenzimidamide* (**7e**). From 6.95 mmol of **2a** and *N*-methylaniline: 2.30 g (84%). M.p. 108–109° (dec.; EtOH). IR: 3420*w* (br.), 3248*m*, 3188*m*, 3114*w*, 3055*m*, 1619*s*, 1593*s*, 1574*s*, 1538*s*, 1491*s*, 1474*m*, 1440*s*, 1382*s*, 1331*s*, 1312*s*, 1297*m*, 1273*m*, 1208*m*, 1118*m*, 1085*s*, 1026*w*, 1001*w*. ^{1}H-NMR: 12.40 (br. *s*, 0.25 H, NH); 10.80 (br. *s*, 0.75 H, NH); 7.57–6.83 (*m*, 15 arom. H); 3.81 (*s*, 2.25 H, MeN); 3.65 (*s*, 0.75 H, MeN). ^{13}C-NMR: 187.3, 155.7 (2*s*, CSe, CN_2); 145.9, 138.6, 134.2 (3*s*, 3 arom. C); 130.7, 129.4, 129.1, 128.9, 127.9, 127.4, 125.7, 124.6, 122.4 (9*d*, 15 arom. C); 45.2 (*q*, MeN). CI-MS: 394 (84, $[M+1]^+$), 315 (49), 273 (45), 108 (100). Anal. calc. for $C_{21}H_{19}N_3Se$ (392.36): C 64.29, H 4.85, N 10.71; found: C 64.12, H 4.77, N 10.69.

4-Methyl-N^2-*[(morpholin-4-yl)(selenocarbonyl)]*-N^1-*phenylbenzimidamide* (**7f**). From 19.7 mmol of **2b** and morpholine: 6.47 g (85%). M.p. 178–179° (dec.; acetone). IR: 3442*w* (br.), 3214*m*, 3180*m*, 3112*m*, 3075*m*, 2980*m*, 2952*m*, 2917*m*, 2852*m*, 1606*s*, 1587*s*, 1527*s*, 1494*s*, 1478*s*, 1429*s*, 1358*m*, 1312*s*, 1277*s*, 1255*m*, 1223*s*, 1208*s*, 1182*m*, 1120*s*, 1080*s*, 1028*m*, 1016*m*. ^{1}H-NMR: 11.50 (*s*, NH); 7.38, 7.12 (*AA′BB′*, *J* = 8.2, 4 arom. H); 7.22 (*t*-like, 2 arom. H); 7.08 (*t*-like, 1 arom. H); 7.04 (*d*-like, 2 arom. H); 4.34, 4.10 (2*t*, *J* = 4.9, 2 CH_2O); 3.78, 3.70 (2*t*, *J* = 4.9, 2 CH_2N); 2.34 (*s*, Me). ^{13}C-NMR: 184.6, 158.7 (2*s*, CSe, CN_2); 141.4, 138.4, 132.0 (3*s*, 3 arom. C); 129.1, 129.0, 128.9, 124.9, 122.8 (5*d*, 9 arom. C); 66.7, 66.3 (2*t*, 2 CH_2O); 51.0, 48.2 (2*t*, 2 CH_2N); 21.4 (*q*, Me). CI-MS: 388 (100, $[M+1]^+$), 308 (90). Anal. calc. for $C_{19}H_{21}N_3OSe$ (386.36): C 59.07, H 5.44, N 10.88; found: C 58.83, H 5.58, N 10.75.

Suitable crystals for the X-ray crystal-structure determination were grown from acetone.

N^2-*[Amino(selenocarbonyl)]*-*4-methyl*-N^1-*phenylbenzimidamide* (**7g**). From 10.8 mmol of **2b** and NH_3: 2.05 g (60%). M.p. 170° (dec., acetone). IR: 3430*w* (sh.), 3235*s*, 3064*m*, 1638*s*, 1597*s*, 1511*s*, 1484*s*, 1447*m*, 1283*m*, 1257*s*, 1224*m*, 1184*s*, 1112*s*, 1071*w*, 1026*m*. ^{1}H-NMR: 11.80, 8.51, 7.85 (3*s*, 3 NH); 7.17–7.07 (*m*, 6 arom. H); 6.97 (*t*-like, 1 arom. H); 6.67 (*d*-like, 2 arom. H); 2.31 (*s*, Me). ^{13}C-NMR: 180.5, 155.3 (2*s*, CSe, CN_2); 146.3, 141.1, 128.4 (3*s*, 3 arom. C); 129.4, 128.7, 128.0, 123.9, 121.9 (5*d*, 9 arom. C); 21.3 (*q*, Me). CI-MS: 318 (40, $[M+1]^+$), 236 (100), 211 (74). Anal. calc. for $C_{15}H_{15}N_3Se$ (316.27): C 56.96, H 4.75, N 13.29; found: C 56.67, H 4.77, N 13.08.

N^2-*[(Benzylamino)(selenocarbonyl)]-4-methyl*-N^1-*phenylbenzimidamide* (**7h**). From 7.3 mmol of **2b** and $PhCH_2NH_2$: 2.84 g (95%). M.p. 153–154° (acetone). IR: 3422*w* (br.), 3175*m*, 3134*m*, 3057*m*, 3021*m*, 2946*m*, 2913*m*, 1638*s*, 1597*m*, 1558*s*, 1526*s*, 1485*s*, 1452*m*, 1372*w*, 1341*m*, 1294*m*, 1273*s*, 1200*m*, 1174*s*, 1112*w*, 1084*w*, 1072*w*, 1026*w*. ^{1}H-NMR: 13.00, 8.50 (2*s*, 2 NH); 7.43–7.23 (*m*, 5 arom. H); 7.12–7.04 (*m*, 6 arom. H); 6.93 (*t*-like, 1 arom. H); 6.61 (*d*-like, 2 arom. H); 5.00 (*d*-like, $PhCH_2$); 2.28 (*s*, Me). ^{13}C-NMR: 180.2, 155.9 (2*s*, CSe, CN_2); 146.1, 141.0, 136.3 (3*s*, 4 arom. C); 129.4, 128.70, 128.68, 128.0, 127.7, 127.6, 123.9, 122.2 (8*d*, 14 arom. C); 52.7 (*t*, CH_2N); 21.3 (*q*, Me). CI-MS: 408 (100, $[M+1]^+$), 326 (69), 236 (28), 211 (50). Anal. calc. for $C_{22}H_{21}N_3Se$ (406.39): C 65.02, H 5.17, N 10.34; found: C 64.91, H 5.24, N 10.34.

N^1-*[[(Methyl)(phenyl)amino](selenocarbonyl)]*-N^2-*phenylbenzimidamide* (**7i**). From 3.75 mmol of **2b** and *N*-methylaniline: 1.22 g (85%). M.p. 117.5–118.5° (AcOEt). IR: 3417*w* (br.), 3238*m*, 3187*m*, 3120*w*, 3046*m*, 1621*s*, 1591*s*, 1534*s*, 1494*s*, 1440*s*, 1385*s*, 1327*s*, 1312*s*, 1271*s*, 1204*m*, 1184*m*, 1114*m*, 1085*s*, 1071*s*, 1028*m*. ^{1}H-NMR: 12.40 (br. *s*, 0.25 H, NH); 10.90 (br. *s*, 0.75 H, NH); 7.46–6.85 (*m*, 14 arom. H); 3.84 (*s*, 2.25 H, MeN); 3.69 (*s*, 0.75 H, MeN); 2.37 (*s*, 0.75 H, Me); 2.26 (*s*, 2.25 H, Me). ^{13}C-NMR (major isomer)[10]): 187.1, 155.9 (2*s*, CSe, CN_2); 146.0, 141.2, 138.8, 131.3 (4*s*, 4 arom. C); 129.5, 129.0, 128.8, 128.6, 127.4, 127.3, 125.8, 124.4, 122.3 (9*d*, 14 arom. C); 45.2 (*q*, MeN); 21.3 (*q*, Me). CI-MS: 408 (17, $[M+1]^+$), 328 (51), 108 (100). Anal. calc. for $C_{22}H_{21}N_3Se$ (406.39): C 65.02, H 5.17, N 10.34; found: C 64.88, H 5.12, N 10.39.

4-Chloro-N^2-*[(morpholin-4-yl)(selenocarbonyl)]*-N^1-*phenylbenzimidamide* (**7j**). From 15.3 mmol of **2c** and morpholine: 5.12 g (82%). M.p. 208–209° (dec.; acetone). IR: 3450*w* (br.), 3176*m*, 3112*m*, 3046*m*, 2954*m*, 2864*m*, 1610*s*, 1583*s*, 1531*s*, 1496*s*, 1432*s*, 1398*m*, 1374*m*, 1310*m*, 1291*m*, 1278*s*, 1253*m*, 1224*s*, 1208*m*, 1176*m*, 1119*m*, 1089*s*, 1076*s*, 1029*m*, 1010*m*. ^{1}H-NMR: 12.00 (*s*, NH); 7.41 (*AA′* of *AA′BB′*, $J=8.5$, 2 arom. H); 7.30–7.18 (*m*, 4 arom. H); 7.10 (*t*-like, 1 arom. H); 6.97 (*d*-like, 2 arom. H); 4.36, 4.12 (2*t*, $J=4.8$, 2 CH_2O); 3.81, 3.72 (2*t*, $J=4.9$, 2 CH_2N). ^{13}C-NMR: 184.4, 158.3 (2*s*, CSe, CN_2); 138.0, 137.0, 133.5 (3*s*, 3 arom. C); 130.6, 129.1, 128.6, 125.4, 123.2 (5*d*, 9 arom. C); 66.7, 66.3 (2*t*, 2 CH_2O); 50.9, 48.4 (2*t*, 2 CH_2N). EI-MS: 407 (11, $M^{+\bullet}$), 326 (8), 241 (20), 214 (34), 86 (40), 77 (100). Anal. calc. for $C_{18}H_{18}ClN_3OSe$ (406.77): C 53.14, H 4.43, Cl 8.73, N 10.33; found: C 52.96, H 4.52, Cl 9.03, N 10.24.

4-Chloro-N^2-*[(dibutylamino)(selenocarbonyl)]*-N^1-*phenylbenzimidamide* (**7k**). From 10.1 mmol of **2c** and Bu_2NH: 4.40 g (97%). M.p. 116.7–117.5° (Et_2O). IR: 3464*w* (sh.), 3238*m*, 3184*m*, 3120*m*, 3054*m*, 2955*s*, 2930*m*, 2870*m*, 1621*s*, 1586*s*, 1566*m*, 1540*s*, 1493*s*, 1441*s*, 1418*s*, 1398*m*, 1370*m*, 1352*m*, 1318*s*, 1262*s*, 1226*m*, 1208*m*, 1199*m*, 1178*m*, 1138*m*, 1097*s*, 1075*m*, 1014*m*. ^{1}H-NMR: 11.40 (*s*, NH); 7.43, 7.26 (*AA′BB′*, $J=8.6$, 4 arom. H); 7.19 (*t*-like, 2 arom. H); 7.05 (*t*-like, 1 arom. H); 6.90 (*d*-like, 2 arom. H); 3.97, 3.79 (2*t*, $J=7.8$, 2 CH_2N); 1.8–1.7, 1.7–1.6 (2*m*, 2 CH_2); 1.50–1.25 (*m*, 2 CH_2); 0.98, 0.93 (2*t*, $J=7.3$, 2 Me). ^{13}C-NMR: 183.7, 155.9 (2*s*, CSe, CN_2); 138.5, 136.7, 133.6 (3*s*, 3 arom. C); 130.6, 129.0, 128.4, 124.7, 122.8 (5*d*, 9 arom. C); 53.9, 51.0 (2*t*, 2 CH_2N); 30.2, 29.0, 20.3, 20.1 (4*t*, 4 CH_2); 13.80, 13.77 (2*q*, 2 Me). CI-MS: 450 (53, $[M+1]^+$), 370 (100). Anal. calc. for $C_{22}H_{28}ClN_3Se$ (448.90): C 58.86, H 6.24, Cl 7.92, N 9.36; found: C 58.63, H 6.39, Cl 8.08, N 9.35.

N^2-*[Amino(selenocarbonyl)]-4-chloro*-N^1-*phenylbenzimidamide* (**7l**). From 2.8 mmol of **2c** and NH_3: 0.70 g (75%). M.p. 190° (dec.; acetone). IR: 3430*w* (sh.), 3237*s* (br.), 3066*m*, 1641*s*, 1599*s*, 1510*s*, 1482*s*, 1449*m*, 1400*m*, 1283*s*, 1259*s*, 1224*s*, 1178*m*, 1114*s*, 1092*s*, 1074*m*, 1027*w*, 1014*m*. ^{1}H-NMR (major isomer)[11]): 9.85, 8.95, 8.82 (3*s*, 3 NH); 7.67–7.55 (*m*, 5 arom. H); 7.38–7.30 (*m*, 2 arom. H); 7.16–7.05 (*m*, 2 arom. H). ^{13}C-NMR (major isomer): 191.1, 150.5 (2*s*, CSe, CN_2); 139.4, 135.2, 132.7 (3*s*, 3 arom. C); 130.2, 128.5, 128.2, 123.8, 120.7 (5*d*, 9 arom. C). CI-MS: 338 (31, $[M+1]^+$), 256 (100). Anal. calc. for $C_{14}H_{12}ClN_3Se$ (336.68): C 49.93, H 3.57, Cl 10.55, N 12.48; found: C 49.96, H 3.58, Cl 10.68, N 12.48.

4-Chloro-N^1-*[[(methyl)(phenyl)amino](selenocarbonyl)]*-N^2-*phenylbenzimidamide* (**7m**). From 19.4 mmol of **2c** and *N*-methylaniline: 7.60 g (92%). M.p. 160° (dec.; AcOEt). IR: 3428*w* (br.), 3235*w*, 3185*m*, 3112*m*, 3054*m*, 1621*s*, 1588*s*, 1567*m*, 1542*s*, 1494*s*, 1442*s*, 1391*s*, 1345*s*, 1275*s*, 1248*m*, 1210*s*, 1180*m*, 1092*s*, 1028*w*, 1014*m*. ^{1}H-NMR: 12.70 (br. *s*, 0.2 H, NH); 11.10 (br. *s*, 0.8 H, NH); 7.51–6.81 (*m*, 14 arom. H); 3.82 (*s*, 2.4 H, MeN); 3.65 (*s*, 0.6 H, MeN). ^{13}C-NMR (major isomer)[10]): 187.1, 155.0 (2*s*, CSe, CN_2); 146.0, 138.4, 136.9, 132.7 (4*s*, 4 arom. C); 130.9, 129.1, 129.0, 128.2, 127.4, 125.7, 124.8, 122.6 (8*d*, 14 arom. C); 45.1 (*q*, MeN). CI-MS: 428 (100, $[M+1]^+$), 348 (53), 216 (26), 108 (43). Anal. calc. for $C_{21}H_{18}ClN_3Se$ (426.81): C 59.09, H 4.22, Cl 8.32, N 9.85; found: C 58.86, H 4.45, Cl 8.47, N 9.79.

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[10]) All signals are doubled; ratio *ca.* 3:1.

[11]) There are signals of two isomers present. The second isomer shows signals for NH at 11.32, 10.78, and 9.97 ppm, and for arom. H at 7.25 (*d*-like, 2 H), 6.90 (*t*-like, 1 H), and 6.68 (*d*-like, 2 H); ratio of the isomers *ca.* 3:1.

4. *Preparation of 1,3-Selenazoles* **9**: *General Procedure A*. To a stirred soln. of **7** in acetone, 1 equiv. of bromide ($BrCH_2Z$) was added at r.t. Within a few min, the iminium salt was precipitated. The mixture was concentrated *i.v.*, and the precipitate was filtered. The solid was suspended in acetone, and 1.1–1.3 equiv. of Et_3N or NaH was added. After a few min, a clear soln. was formed, and then a solid precipitated. After stirring for 10–30 min, the mixture was poured into ice/H_2O, and stirred for another 10 min to 1 h. The precipitate was filtered by suction and air-dried. For anal. purposes, an aliquot was recrystallized to give white or yellowish crystals.

General Procedure B. A soln. of isoselenocyanate **2** in acetone was treated subsequently with an amine according to *Sect. 3* and with $BrCH_2Z$ according to *General Procedure A* in *Sect. 4*.

[2-(Morpholin-4-yl)-4-phenyl-1,3-selenazol-5-yl](4-nitrophenyl)methanone (**9a**). From 2.8 mmol of **7a** and 4-nitrophenacyl bromide (=2-bromo-1-(4-nitrophenyl)ethanone): 1.10 g (90%). M.p. 196.4–197.4° (EtOH). IR: 3063*w*, 2972*w*, 2950*w*, 2896*w*, 2858*w*, 1609*s*, 1592*s*, 1546*s*, 1518*s*, 1472*s*, 1441*s*, 1386*w*, 1370*m*, 1341*s*, 1286*s*, 1261*s*, 1225*m*, 1172*w*, 1157*w*, 1116*s*, 1066*m*, 1032*m*, 1012*m*. ^{1}H-NMR: 7.85, 7.46 (*AA′BB′*, J = 8.9, 4 arom. H); 7.23–7.18 (*m*, 2 arom. H); 7.14–7.07 (*m*, 1 arom. H); 7.04–6.97 (*m*, 2 arom. H); 3.83 (*t*, J = 4.9, 2 CH_2O); 3.66 (*t*, J = 4.9, 2 CH_2N). ^{13}C-NMR: 187.8 (*s*, CO); 174.4, 161.7, 128.0 (3*s*, C(2), C(4), C(5)); 148.5, 143.8, 135.2 (3*s*, 3 arom. C); 129.9, 129.6, 129.1, 127.6, 122.5 (5*d*, 9 arom. C); 66.0 (*t*, 2 CH_2O); 49.4 (*t*, 2 CH_2N). APCI-MS (MeOH/H_2O/NH_4OAc): 444 ([M + 1]$^+$). Anal. calc. for $C_{20}H_{17}N_3O_4Se$ (442.34): C 54.30, H 3.85, N 9.50; found: C 54.22, H 4.02, N 9.49.

[4-Phenyl-2-(pyrrolidin-1-yl)-1,3-selenazol-5-yl](4-nitrophenyl)methanone (**9b**). From 1.4 mmol of **7b** and 4-nitrophenacyl bromide: 0.58 g (97%). M.p. 219.1–219.8° (acetone). IR: 3076*w*, 2981*w*, 2947*w*, 2887*w*, 2840*w*, 1607*m*, 1584*s*, 1557*s*, 1517*s*, 1503*s*, 1473*s*, 1442*m*, 1406*w*, 1343*s*, 1327*s*, 1312*s*, 1286*s*, 1267*s*, 1244*m*, 1178*w*, 1140*w*, 1101*m*, 1076*w*, 1026*w*, 1013*w*. ^{1}H-NMR (235 K): 7.84, 7.39 (*AA′BB′*, J = 8.9, 4 arom. H); 7.17 (*d*-like, 2 arom. H); 7.07 (*t*-like, 1 arom. H); 6.98 (*t*-like, 2 arom. H); 3.79, 3.38 (2*t*, J = 6.4, 2 CH_2N); 2.18, 2.10 (2 *quint.*, J = 6.6, 2 CH_2). ^{13}C-NMR (235 K): 187.7 (*s*, CO); 170.4, 163.0, 127.0 (3*s*, C(2), C(4), C(5)); 147.5, 144.0, 134.8 (3*s*, 3 arom. C); 129.7, 129.4, 129.0, 127.6, 122.4 (5*d*, 9 arom. C); 52.3, 49.4 (2*t*, 2 CH_2N); 25.7, 25.4 (2*t*, 2 CH_2). EI-MS: 427 (48, $M^{+\bullet}$), 398 (10), 304 (13), 181 (44), 179 (20), 177 (11), 176 (12), 150 (73), 129 (24), 120 (30), 104 (100). Anal. calc. for $C_{20}H_{17}N_3O_3Se$ (426.34): C 56.34, H 3.99, N 9.86; found: C 56.22, H 4.01, N 9.80.

{2-[(Methyl)(phenyl)amino]-4-phenyl-1,3-selenazol-5-yl}(4-nitrophenyl)methanone (**9c**). From 2.8 mmol of **7e** and 4-nitrophenacyl bromide: 1.23 g (95%). M.p. 178.7–179.3° (EtOH). IR: 3057*w*, 2933*w*, 1608*m*, 1592*s*, 1510*s* (br.), 1472*s*, 1453*s*, 1403*s*, 1343*s*, 1335*s*, 1305*s*, 1289*s*, 1165*m*, 1127*m*, 1100*m*, 1012*m*. ^{1}H-NMR: 7.84 (*AA′* of *AA′BB′*, J = 8.9, 2 arom. H); 7.53–7.37 (*m*, 7 arom. H); 7.29–7.23 (*m*, 2 arom. H); 7.12–7.07 (*m*, 1 arom. H); 7.05–6.95 (*m*, 2 arom. H); 3.63 (*s*, MeN). ^{13}C-NMR: 188.0 (*s*, CO); 174.5, 161.4, 127.56 (3*s*, C(2), C(4), C(5)); 148.4, 146.4, 144.0, 135.4 (4*s*, 4 arom. C); 130.4, 130.0, 129.6, 129.0, 128.4, 127.64, 125.3, 122.5 (8*d*, 14 arom. C); 40.3 (*q*, MeN). APCI-MS (MeOH/H_2O/NH_4OAc): 464 ([M + 1]$^+$). Anal. calc. for $C_{23}H_{17}N_3O_3Se$ (462.37): C 59.74, H 3.68, N 9.09; found: C 59.58, H 3.68, N 9.08.

Suitable crystals for the X-ray crystal-structure determination were grown from EtOH.

(4-Methoxyphenyl)[4-phenyl-2-(piperidin-1-yl)-1,3-selenazol-5-yl]methanone (**9d**). From 4.3 mmol of **7c** and 4-methoxyphenacyl bromide: 1.80 g (98%). M.p. 158–159° (acetone). IR: 3006*w*, 2966*w*, 2945*m*, 2859*w*, 2840*w*, 1605*s*, 1588*s*, 1572*m*, 1535*s*, 1506*s*, 1470*s*, 1444*s*, 1339*s*, 1305*s*, 1282*s*, 1249*s*, 1170*m*, 1131*m*, 1105*m*, 1072*w*, 1033*m*, 1024*m*, 1008*m*. ^{1}H-NMR: 7.44, 6.54 (*AA′BB′*, J = 8.9, 4 arom. H); 7.33 (*dd*-like, 2 arom. H); 7.12–7.01 (*m*, 3 arom. H); 3.69 (*s*, MeO); 3.57 (br. *s*, 2 CH_2N); 1.68 (br. *s*, 3 CH_2). ^{13}C-NMR: 188.9 (*s*, CO); 173.0, 161.9, 127.0 (3*s*, C(2), C(4), C(5)); 159.1, 136.1, 130.9 (3*s*, 3 arom. C); 131.3, 129.9, 128.1, 127.4, 112.7 (5*d*, 9 arom. C); 55.2 (*q*, MeO); 50.5 (*t*, 2 CH_2N); 25.2 (*t*, 2 CH_2); 24.0 (*t*, CH_2). CI-MS: 427 (100, [M + 1]$^+$), 236 (50). Anal. calc. for $C_{22}H_{22}N_2O_2Se$ (425.39): C 62.12, H 5.18, N 6.59; found: C 62.06, H 5.28, N 6.58.

Suitable crystals for the X-ray crystal-structure determination were grown from acetone.

Ethyl 2-(Morpholin-4-yl)-4-phenyl-1,3-selenazole-5-carboxylate (**9e**). From 12.5 mmol of **7a** and ethyl 2-bromoacetate: 4.00 g (88%). M.p. 97.7–98.5° (hexane/Et_2O). IR: 3068*w*, 3025*w*, 2982*m*, 2905*m*, 2861*m*, 1667*s*, 1530*s*, 1483*s*, 1448*m*, 1392*m*, 1366*s*, 1309*s*, 1298*s*, 1256*s*, 1231*s*, 1192*w*, 1137*m*, 1111*s*, 1067*s*, 1031*m*, 1021*m*. ^{1}H-NMR: 7.70–7.64 (*m*, 2 arom. H); 7.38–7.34 (*m*, 3 arom. H); 4.16 (*q*, J = 7.1, MeCH_2O); 3.79 (*t*, J = 4.9, 2 CH_2O); 3.55 (*t*, J = 4.9, 2 CH_2N); 1.20 (*t*, J = 7.1, Me). ^{13}C-NMR: 163.3 (*s*, CO); 173.2, 160.7, 115.0 (3*s*, C(2), C(4), C(5)); 135.6 (*s*, 1 arom. C); 129.8, 128.8, 127.5 (3*d*, 5 arom. C); 66.1 (*t*, 2 CH_2O); 60.7 (*t*, MeCH_2O); 49.3 (*t*, 2 CH_2N); 14.2 (*q*, Me). CI-MS: 367 ([M + 1]$^+$). Anal. calc. for $C_{16}H_{18}N_2O_3Se$ (365.29): C 52.60, H 4.93, N 7.67; found: C 52.56, H 5.06, N 7.68.

Ethyl 4-Phenyl-2-(pyrrolidin-4-yl)-4-phenyl-1,3-selenazole-5-carboxylate (**9f**). From 1.4 mmol of **7b** and ethyl 2-bromoacetate: 0.40 g (80%). M.p. 111.5–112.5° (Et_2O). IR: 3047*w*, 2970*m*, 2951*m*, 2900*w*, 2871*m*, 2852*m*, 1657*s*, 1600*w*, 1552*s*, 1515*s*, 1480*s*, 1447*m*, 1391*w*, 1366*m*, 1340*m*, 1319*s*, 1305*s*, 1282*s*, 1264*s*, 1242*s*, 1185*m*,

1171*m*, 1126*m*, 1066*s*, 1026*m*. ^{1}H-NMR: 7.70–7.65 (*m*, 2 arom. H); 7.38–7.34 (*m*, 3 arom. H); 4.14 (*q*, *J* = 7.1, CH_2O); 3.48 (br.*s*, 2 CH_2N); 2.10–2.00 (*m*, 2 CH_2); 1.19 (*t*, *J* = 7.1, Me). ^{13}C-NMR: 163.4 (*s*, CO); 169.1, 161.4, 113.5 (3*s*, C(2), C(4), C(5)); 136.0 (*s*, 1 arom. C); 129.7, 128.5, 127.4 (3*d*, 5 arom. C); 60.3 (*t*, CH_2O); 50.4 (*t*, 2 CH_2N); 25.5 (*t*, 2 CH_2); 14.2 (*q*, Me). ESI-MS (MeOH): 351 ($[M+1]^+$). Anal. calc. for $C_{16}H_{18}N_2O_2Se$ (349.29): C 55.01, H 5.16, N 8.02; found: C 54.98, H 5.29, N 8.01.

Ethyl 2-[(Methyl)(phenyl)amino]-4-phenyl-1,3-selenazole-5-carboxylate (**9g**). From 5.85 mmol of **7e** and ethyl 2-bromoacetate: 1.78 g (79%). M.p. 87.5–88.5° (hexane). IR: 3058*w*, 2981*w*, 2938*w*, 2898*w*, 1703*s*, 1597*w*, 1586*w*, 1514*s* (br.), 1496*s*, 1479*s*, 1451*m*, 1406*s*, 1360*w*, 1337*s*, 1335*s*, 1278*s*, 1232*s*, 1180*m*, 1157*w*, 1122*s*, 1054*s*, 1028*m*, 1020*m*. ^{1}H-NMR: 7.76–7.71 (*m*, 2 arom. H); 7.50–7.33 (*m*, 8 arom. H); 4.10 (*q*, *J* = 7.1, CH_2O); 3.57 (*s*, MeN); 1.16 (*t*, *J* = 7.1, Me). ^{13}C-NMR: 163.3 (*s*, CO); 172.8, 160.5, 114.3 (3*s*, C(2), C(4), C(5)); 146.7, 135.7 (2*s*, 2 arom. C); 130.2, 129.7, 128.6, 127.8, 127.4, 125.4 (6*d*, 10 arom. C); 60.4 (*t*, CH_2O); 40.0 (*q*, MeN); 14.4 (*q*, Me). CI-MS: 387 (100, $[M+1]^+$), 349 (10). Anal. calc. for $C_{19}H_{18}N_2O_2Se$ (385.33): C 59.22, H 4.68, N 7.27; found: C 59.25, H 4.76, N 7.33.

2-[(Methyl)(phenyl)amino]-4-phenyl-1,3-selenazole-5-carbonitrile (**9h**). From 2.75 mmol of **7e** and 2-bromoacetonitrile: 0.79 g (85%). M.p. 108–109°. IR: 3055*w*, 2931*w*, 2895*w*, 2190*m*, 1586*w*, 1515*s* (br.), 1496*m*, 1478*s*, 1455*m*, 1440*m*, 1406*s*, 1349*s*, 1327*m*, 1292*m*, 1280*m*, 1266*m*, 1179*w*, 1162*w*, 1154*w*, 1126*w*, 1081*w*, 1028*w*, 1019*w*, 1000*w*. ^{1}H-NMR: 8.12–8.07 (*m*, 2 arom. H); 7.53–7.38 (*m*, 8 arom. H); 3.62 (*s*, MeN). ^{13}C-NMR: 173.2, 162.8 (2*s*, C(2), C(4)); 146.2, 133.7 (2*s*, 2 arom. C); 130.5, 129.6, 128.5, 128.2, 125.3 (5*d*, 10 arom. C); 116.7 (*s*, C≡N); 88.4 (*s*, C(5)); 40.6 (*q*, MeN). CI-MS: 340 ($[M+1]^+$). Anal. calc. for $C_{17}H_{13}N_3Se$ (338.27): C 60.36, H 3.85, N 12.43; found: C 60.45, H 3.80, N 12.34.

[4-(4-Methylphenyl)-2-(morpholin-4-yl)-1,3-selenazol-5-yl]phenylmethanone (**9i**). From 2.5 mmol of **7f** and phenacyl bromide: 1.02 g (96%). M.p. 174.5–175.0° (EtOH). IR: 3022*w*, 2968*m*, 2948*w*, 2861*m*, 1605*s*, 1574*m*, 1541*s*, 1476*s*, 1446*s*, 1428*m*, 1406*w*, 1375*w*, 1321*s*, 1302*s*, 1283*s*, 1260*s*, 1227*s*, 1172*w*, 1180*m*, 1156*w*, 1115*s*, 1100*m*, 1068*m*, 1029*m*. ^{1}H-NMR: 7.42 (*AA′* of *AA′BB′*, *J* = 8.4, 2 arom. H); 7.22–7.16 (*m*, 3 arom. H); 7.05 (*t*-like, 2 arom. H); 6.82 (*d*-like, 2 arom. H); 3.81 (*t*, *J* = 4.9, 2 CH_2O); 3.61 (*t*, *J* = 4.9, 2 CH_2N); 2.18 (*s*, Me). ^{13}C-NMR: 190.2 (*s*, CO); 173.6, 159.9, 127.8 (3*s*, C(2), C(4), C(5)); 138.4, 138.2, 132.8 (3*s*, 3 arom. C); 130.8, 129.9, 129.1, 128.1, 127.4 (5*d*, 9 arom. C); 66.0 (*t*, 2 CH_2O); 49.2 (*t*, 2 CH_2N); 21.1 (*q*, Me). EI-MS: 412 (17, $M^{+\cdot}$), 114 (25), 105 (75), 77 (100). Anal. calc. for $C_{21}H_{20}N_2O_2Se$ (411.37): C 61.31, H 4.87, N 6.81; found: C 61.21, H 4.75, N 6.79.

[4-(4-Methylphenyl)-2-(morpholin-4-yl)-1,3-selenazol-5-yl](4-nitrophenyl)methanone (**9j**). From 2.4 mmol of **7f** and 4-nitrophenacyl bromide: 1.03 g (95%). M.p. 194–194.5° (EtOH). IR: 3080*w*, 2966*w*, 2916*w*, 2858*m*, 1608*s*, 1590*s*, 1514*s*, 1473*s*, 1446*s*, 1435*s*, 1406*w*, 1331*s*, 1308*s*, 1291*s*, 1263*s*, 1230*s*, 1184*w*, 1148*w*, 1119*s*, 1100*m*, 1071*w*, 1036*m*, 1022*m*. ^{1}H-NMR: 7.86, 7.46 (*AA′BB′*, *J* = 8.8, 4 arom. H); 7.09, 6.81 (*AA′BB′*, *J* = 8.0, 4 arom. H); 3.83 (*t*, *J* = 4.9, 2 CH_2O); 3.66 (*t*, *J* = 4.9, 2 CH_2N); 2.17 (*s*, Me). ^{13}C-NMR: 187.8 (*s*, CO); 174.2, 162.0, 127.8 (3*s*, C(2), C(4), C(5)); 148.3, 143.9, 139.5, 132.4 (4*s*, 4 arom. C); 129.9, 129.6, 128.3, 122.5 (4*d*, 8 arom. C); 66.0 (*t*, 2 CH_2O); 49.4 (*t*, 2 CH_2N); 21.0 (*q*, Me). CI-MS: 458 (74, $[M+1]^+$), 428 (100). Anal. calc. for $C_{21}H_{19}N_3O_4Se$ (456.34): C 55.26, H 4.17, N 9.21; found: C 55.08, H 4.22, N 9.13.

4-(4-Methylphenyl)-2-(morpholin-4-yl)-1,3-selenazole-5-carboxamide (**9k**). From 2.8 mmol of **7f** and 2-bromoacetamide: 0.80 g (81%). M.p. 230.5–231.5° (acetone). IR: 3436*s*, 3296*m*, 3158*s*, 2957*m*, 2914*m*, 2849*m*, 1639*s*, 1580*s*, 1531*s*, 1493*s*, 1447*m*, 1433*m*, 1398*s*, 1318*s*, 1268*s*, 1231*s*, 1182*m*, 1137*m*, 1118*s*, 1070*w*, 1031*m*. ^{1}H-NMR: 7.45, 7.25 (*AA′BB′*, *J* = 8.0, 4 arom. H); 5.60 (*s*, 2 H); 3.78 (*t*, *J* = 4.9, 2 CH_2O); 3.52 (*t*, *J* = 4.9, 2 CH_2N); 2.39 (*s*, Me). ^{13}C-NMR: 172.9, 165.1, 123.1 (3*s*, C(2), C(4), C(5)); 154.8 (*s*, CO); 139.4, 132.3 (2*s*, 2 arom. C); 129.7, 128.9 (2*d*, 4 arom. C); 66.0 (*t*, 2 CH_2O); 49.0 (*t*, 2 CH_2N); 21.3 (*q*, Me). CI-MS: 352 ($[M+1]^+$). Anal. calc. for $C_{15}H_{17}N_3O_2Se$ (350.28): C 51.43, H 4.86, N 12.00; found: C 51.45, H 4.92, N 12.09.

Ethyl 4-(4-Methylphenyl)-2-(morpholin-4-yl)-1,3-selenazole-5-carboxylate (**9l**). From 5.0 mmol of **7f** and ethyl 2-bromoacetate: 1.60 g (85%). M.p. 130–130.6° (acetone). IR: 2980*m*, 2905*m*, 2863*m*, 1700*m*, 1666*s*, 1612*w*, 1530*s*, 1489*s*, 1448*m*, 1393*m*, 1366*s*, 1318*s*, 1307*s*, 1288*s*, 1257*s*, 1232*s*, 1212*m*, 1192*m*, 1137*m*, 1113*s*, 1068*s*, 1022*m*. ^{1}H-NMR: 7.59, 7.17 (*AA′BB′*, *J* = 8.1, 4 arom. H); 4.16 (*q*, *J* = 7.1, MeCH_2O); 3.77 (*t*, *J* = 4.9, 2 CH_2O); 3.65 (*t*, *J* = 4.9, 2 CH_2N); 2.36 (*s*, Me); 1.22 (*t*, *J* = 7.1, Me). ^{13}C-NMR: 163.2 (*s*, CO); 173.0, 160.8, 114.3 (3*s*, C(2), C(4), C(5)); 138.6, 132.6 (2*s*, 2 arom. C); 129.6, 128.1 (2*d*, 4 arom. C); 66.0 (*t*, 2 CH_2O); 60.5 (*t*, MeCH_2O); 49.1 (*t*, 2 CH_2N); 21.3 (*q*, Me); 14.2 (*q*, Me). CI-MS: 381 (100, $[M+1]^+$), 211 (23), 191 (11). Anal. calc. for $C_{17}H_{20}N_2O_3Se$ (379.32): C 53.83, H 5.28, N 7.39; found: C 53.73, H 5.18, N 7.40.

4-(4-Methylphenyl)-2-[(methyl)(phenyl)amino]-1,3-selenazole-5-carbonitrile (**9m**). From 2.15 mmol of **7i** and 2-bromoacetonitrile: 0.68 g (90%). M.p. 149.5–150°. IR: 3050*w*, 2939*w*, 2194*s*, 1586*w*, 1510*s* (br.), 1494*s*, 1456*s*, 1403*s*, 1349*s*, 1328*m*, 1302*m*, 1276*m*, 1264*m*, 1184*m*, 1116*m*, 1082*m*, 1035*w*, 1018*w*. ^{1}H-NMR: 8.00, 7.25 (*AA′BB′*, *J* = 8.2, 4 arom. H); 7.50 (*t*-like, 2 arom. H); 7.43–7.36 (*m*, 3 arom. H); 3.62 (*s*, MeN); 3.29 (*s*, Me).

^{13}C-NMR: 173.2, 162.9 (2*s*, C(2), C(4)); 146.2, 139.8, 131.1 (3*s*, 3 arom. C); 130.5, 129.2, 128.5, 128.1, 125.3 (5*d*, 10 arom. C); 116.9 (*s*, C≡N); 87.7 (*s*, C(5)); 40.5 (*q*, MeN); 21.1 (*q*, Me). CI-MS: 354 ($[M+1]^+$). Anal. calc. for $C_{18}H_{15}N_3Se$ (352.30): C 61.36, H 4.26, N 11.93; found: C 61.44, H 4.40, N 11.81.

4-[4-(4-Methylphenyl)-2-[(methyl)(phenyl)amino]-1,3-selenazol-5-yl]benzonitrile (**9n**). From 3.7 mmol of **7i** and 4-(bromomethyl)benzonitrile: 1.35 g (86%). M.p. 219.2–220.5°. IR: 3027*w*, 2939*w*, 2224*m*, 1598*m*, 1584*w*, 1522*s*, 1504*s*, 1454*m*, 1403*s*, 1320*m*, 1299*m*, 1262*m*, 1180*w*, 1127*m*, 1103*m*, 1019*w*. ^{1}H-NMR: 7.50–7.30 (*m*, 9 arom. H); 7.21 (*t*-like, 2 arom. H); 7.09 (*d*-like, 2 arom. H); 3.59 (*s*, MeN); 2.34 (*s*, Me). ^{13}C-NMR: 170.0, 149.6 (2*s*, C(2), C(4)); 147.2, 140.4, 137.8, 132.8 (4*s*, 4 arom. C); 132.0, 130.0, 129.6, 129.2, 129.0, 127.3, 125.2 (7*d*, 13 arom. C); 123.2, 109.3 (2*s*, C(5), 1 arom. C); 118.9 (*s*, C≡N); 39.9 (*q*, MeN); 21.2 (*q*, Me). CI-MS: 430 (100, $[M+1]^+$), 349 (59). Anal. calc. for $C_{24}H_{19}N_3Se$ (428.40): C 67.29, H 4.44, N 9.81; found: C 67.08, H 4.50, N 9.72.

[4-(4-Chlorophenyl)-2-(morpholin-4-yl)-1,3-selenazol-5-yl](4-nitrophenyl)methanone (**9o**). From 2.4 mmol of **7j** and 4-nitrophenacyl bromide: 1.10 g (95%). M.p. 234.5–235° (acetone). IR: 3081*w*, 2965*w*, 2919*w*, 2857*w*, 1608*m*, 1588*s*, 1514*s*, 1470*s*, 1446*s*, 1434*s*, 1400*m*, 1349*s*, 1330*s*, 1300*s*, 1289*s*, 1272*s*, 1262*s*, 1232*s*, 1177*w*, 1149*w*, 1119*s*, 1100*m*, 1084*m*, 1038*w*, 1016*m*. ^{1}H-NMR: 7.94, 7.51 (*AA′BB′*, *J* = 8.5, 4 arom. H); 7.19, 7.02 (*AA′BB′*, *J* = 8.3, 4 arom. H); 3.84 (*t*, *J* = 4.7, 2 CH_2O); 3.65 (*t*, *J* = 4.7, 2 CH_2N). ^{13}C-NMR: 187.5 (*s*, CO); 174.3, 160.0, 127.84 (3*s*, C(2), C(4), C(5)); 148.6, 143.7, 135.4, 133.6 (4*s*, 4 arom. C); 131.1, 129.7, 127.85, 122.7 (4*d*, 8 arom. C); 66.0 (*t*, 2 CH_2O); 49.4 (*t*, 2 CH_2N). CI-MS: 478 (100, $[M+1]^+$), 448 (66). Anal. calc. for $C_{20}H_{16}ClN_3O_4Se$ (476.78): C 50.37, H 3.36, Cl 7.45, N 8.81; found: C 50.30, H 3.47, Cl 7.61, N 8.79.

[4-(4-Chlorophenyl)-2-(dibutylamino)-1,3-selenazol-5-yl](4-nitrophenyl)methanone (**9p**). From 1.7 mmol of **7k** and 4-nitrophenacyl bromide: 0.82 g (92%). M.p. 131.5–132° (Et_2O). IR: 3053*w*, 2956*m*, 2930*m*, 2862*m*, 1598*w*, 1584*s*, 1539*s*, 1504*s*, 1465*s*, 1402*m*, 1329*s*, 1290*s*, 1240*m*, 1178*w*, 1155*w*, 1101*m*, 1014*m*. ^{1}H-NMR: 7.93, 7.50 (*AA′BB′*, *J* = 8.9, 4 arom. H); 7.18, 7.00 (*AA′BB′*, *J* = 8.6, 4 arom. H); 3.51 (br. *s*, 2 CH_2N); 1.72 (*quint.*, *J* = 7.5, 4 H); 1.27 (*sext.*, *J* = 7.4, 4 H); 0.98 (*t*, *J* = 7.3, 2 Me). ^{13}C-NMR: 187.1 (*s*, CO); 173.3, 169.7, 126.5 (3*s*, C(2), C(4), C(5)); 148.4, 144.3, 135.1, 134.0 (4*s*, 4 arom. C); 131.2, 129.6, 127.7, 122.7 (4*d*, 8 arom. C); 55–50 (very br., 2 CH_2N); 29.2, 20.0 (2*t*, 4 CH_2); 13.7 (*q*, 2 Me). CI-MS: 420 (100, $[M+1]^+$), 490 (20). Anal. calc. for $C_{24}H_{26}ClN_3O_3Se$ (518.90): C 55.54, H 5.01, Cl 6.85, N 8.10; found: C 55.68, H 5.21, Cl 6.92, N 8.01.

{4-(4-Chlorophenyl)-2-[(methyl)(phenyl)amino]-1,3-selenazol-5-yl}(4-nitrophenyl)methanone (**9q**). From 2.3 mmol of **7m** and 4-nitrophenacyl bromide: 1.15 g (99%). M.p. 193–194° (acetone). IR: 3065*w*, 2939*w*, 2855*w*, 1613*s*, 1593*s*, 1570*m*, 1522*s*, 1467*s*, 1400*s*, 1322*s* (br.), 1301*s* (br.), 1161*m*, 1102*m*, 1084*m*, 1015*m*. ^{1}H-NMR: 7.93 (*AA′* of *AA′BB′*, *J* = 8.8, 2 arom. H); 7.54–7.38 (*m*, 7 arom. H); 7.25, 7.04 (*AA′BB′*, *J* = 8.5, 4 arom. H); 3.63 (*s*, MeN). ^{13}C-NMR: 187.8 (*s*, CO); 174.7, 156.7, 127.4 (3*s*, C(2), C(4), C(5)); 148.8, 146.3, 144.1, 135.3, 134.0 (5*s*, 5 arom. C); 131.3, 130.6, 129.8, 128.6, 128.0, 125.4, 122.9 (7*d*, 13 arom. C); 40.4 (*q*, MeN). EI-MS: 497 (30, $M^{+\bullet}$), 375 (5), 215 (26), 180 (14), 150 (74), 132 (12), 123 (12), 120 (31), 106 (97), 105 (21), 104 (100), 92 (57), 91 (67). Anal. calc. for $C_{23}H_{16}ClN_3O_3Se$ (496.81): C 55.59, H 3.22, Cl 7.15, N 8.46; found: C 55.42, H 3.23, Cl 7.39, N 8.62.

Ethyl 4-(4-Chlorophenyl)-2-(dibutylamino)-1,3-selenazole-5-carboxylate (**9r**). From 6.25 mmol of **7k** and ethyl 2-bromoacetate: 2.60 g (94%). Yellowish oil. IR (film): 2957*s*, 2931*m*, 2871*m*, 1699*s*, 1670*m*, 1595*w*, 1534*s*, 1478*s*, 1399*m*, 1362*m*, 1326*s*, 1294*s*, 1271*s*, 1233*s*, 1187*m*, 1123*s*, 1090*s*, 1056*s*, 1015*m*. ^{1}H-NMR: 7.67, 7.33 (*AA′BB′*, *J* = 8.6, 4 arom. H); 4.16 (*q*, *J* = 7.1, CH_2O); 3.44 (br. *t*, 2 CH_2N); 1.67 (*quint.*, *J* = 7.5, 4 H); 1.37 (*sext.*, *J* = 7.4, 4 H); 1.23 (*t*, *J* = 7.1, Me); 0.96 (*t*, *J* = 7.3, 2 Me). ^{13}C-NMR: 171.8 (*s*, CO); 163.3, 159.6, 112.8 (3*s*, C(2), C(4), C(5)); 134.4, 134.1 (2*s*, 2 arom. C); 131.3, 127.4 (2*d*, 4 arom. C); 60.5 (*t*, CH_2O); 52.3 (very br., 2 CH_2N); 29.2, 20.0 (2*t*, 4 CH_2); 14.2 (*q*, Me); 13.7 (*q*, 2 Me). CI-MS: 443 ($[M+1]^+$). Anal. calc. for $C_{20}H_{27}ClN_2O_2Se$ (441.86): C 54.36, H 6.12, Cl 8.04, N 6.34; found: C 54.49, H 6.23, Cl 8.09, N 6.48.

Ethyl 4-(4-Chlorophenyl)-2-[(methyl)(phenyl)amino]-1,3-selenazole-5-carboxylate (**9s**). From 4.6 mmol of **7m** and ethyl 2-bromoacetate: 1.65 g (85%). M.p. 140.7–141.2° (Et_2O). IR: 2974*w*, 2932*w*, 1701*s*, 1596*w*, 1584*w*, 1570*w*, 1509*s*, 1493*s*, 1477*s*, 1451*m*, 1400*s*, 1364*m*, 1340*s*, 1304*m*, 1290*m*, 1259*s*, 1241*s*, 1171*m*, 1156*w*, 1133*s*, 1097*m*, 1087*m*, 1058*s*, 1014*m*. ^{1}H-NMR: 7.71 (*AA′* of *AA′BB′*, *J* = 8.4, 2 arom. H); 7.51–7.33 (*m*, 7 arom. H); 4.12 (*q*, *J* = 7.1, CH_2O); 3.56 (*s*, MeN); 1.18 (*t*, *J* = 7.1, Me). ^{13}C-NMR: 172.9 (*s*, CO); 163.2, 159.1, 114.5 (3*s*, C(2), C(4), C(5)); 146.3, 134.5, 134.1 (3*s*, 3 arom. C); 131.2, 130.3, 127.9, 127.6, 125.4 (5*d*, 9 arom. C); 60.6 (*t*, CH_2O); 40.0 (*q*, MeN); 14.1 (*q*, Me). EI-MS: 420 (24, $M^{+\bullet}$), 348 (9), 215 (22), 180 (14), 136 (21), 123 (15), 107 (13), 106 (100), 105 (13), 91 (50). Anal. calc. for $C_{19}H_{17}ClN_2O_2Se$ (419.77): C 54.35, H 4.05, Cl 8.46, N 6.67; found: C 54.34, H 4.21, Cl 8.63, N 6.74.

Ethyl 4-(4-Chlorophenyl)-2-(morpholin-4-yl)-1,3-selenazole-5-carboxylate (**9t**). From 4.3 mmol of **7j** and ethyl 2-bromoacetate: 1.66 g (96%). M.p. 145.5–146° (Et_2O). IR: 2988*m*, 2905*m*, 2864*m*, 1700*m*, 1666*s*, 1598*w*, 1572*w*, 1527*s*, 1480*s*, 1447*m*, 1393*m*, 1366*s*, 1314*s*, 1301*s*, 1288*s*, 1272*s*, 1256*s*, 1232*s*, 1192*w*, 1137*m*, 1110*s*, 1094*s*, 1067*s*, 1034*m*, 1020*m*. ^{1}H-NMR: 7.64, 7.34 (*AA′BB′*, *J* = 8.7, 4 arom. H); 4.16 (*q*, *J* = 7.1, MeCH_2O); 3.80 (*t*, *J* =

4.9, 2 CH_2O); 3.54 (t, J = 4.9, 2 CH_2N); 1.23 (t, J = 7.1, Me). ^{13}C-NMR: 163.1 (s, CO); 173.2, 159.2, 115.0 (3s, C(2), C(4), C(5)); 134.6, 133.9 (2s, 2 arom. C); 131.2, 127.6 (2d, 4 arom. C); 66.0 (t, 2 CH_2O); 60.7 (t, MeCH_2O); 49.1 (t, 2 CH_2N); 14.1 (q, Me). CI-MS: 401 ($[M+1]^+$). Anal. calc. for $C_{16}H_{17}ClN_2O_3Se$ (399.74): C 48.06, H 4.26, Cl 8.89, N 7.01; found: C 48.00, H 4.21, Cl 8.98, N 7.06.

4-(4-Chlorophenyl)-2-(morpholin-4-yl)-1,3-selenazole-5-carbonitrile (**9u**). From 2.4 mmol of **7j** and 2-bromoacetonitrile: 0.81 g (95%). M.p. 170–171° (acetone). IR: 2987*w*, 2958*w*, 2917*w*, 2876*w*, 2197*s*, 1596*w*, 1552*s*, 1511*w*, 1476*m*, 1461*w*, 1445*m*, 1400*m*, 1374*w*, 1342*s*, 1330*m*, 1318*m*, 1302*m*, 1272*m*, 1229*m*, 1172*w*, 1118*s*, 1100*m*, 1089*m*, 1069*w*, 1031*m*, 1016*m*. ^{1}H-NMR: 8.00, 7.39 ($AA'BB'$, J = 8.8, 4 arom. H); 3.82 (t, J = 4.9, 2 CH_2O); 3.57 (t, J = 4.9, 2 CH_2N). ^{13}C-NMR: 173.3, 161.5 (2s, C(2), C(4)); 135.7, 131.9 (2s, 2 arom. C); 129.5, 128.7 (2d, 4 arom. C); 116.4 (s, C≡N); 88.9 (s, C(5)); 65.9 (t, 2 CH_2O); 49.6 (t, 2 CH_2N). EI-MS: 353 (23, $M^{+\cdot}$), 296 (17), 241 (23), 163 (33), 162 (19), 161 (100), 126 (20), 114 (13), 111 (10), 99 (13), 86 (11). Anal. calc. for $C_{14}H_{12}ClN_3OSe$ (352.68): C 47.66, H 3.40, Cl 10.07, N 11.91; found: C 47.66, H 3.57, Cl 10.31, N 11.93.

5. *Preparation of 1,3-Selenazoles* **10**: *General Procedure.* A soln. of **7d** or **7l** ($R^2 = R^3 = H$) and 1 equiv. of 4-nitrophenacyl bromide in acetone was heated to reflux for 30 min. Then, the precipitated salt was filtered and triturated in 5% aq. NaOH soln. for 1 h. The solid product was washed with H_2O, filtered by suction, and air-dried. For anal. purposes, an aliquot was recrystallized to give yellowish crystals.

N^2-*[4-(4-Nitrophenyl)-1,3-selenazol-2-yl]*-N^1-*phenylbenzimidamide* (**10a**). From 2.95 mmol of **7d** and 4-nitrophenacyl bromide: 1.30 g (98%). M.p. 218–219° (acetone). IR: 3367*m*, 3329*m*, 3102*w*, 3062*w*, 1638*m*, 1593*s*, 1570*m*, 1537*s*, 1516*s*, 1450*m*, 1407*m*, 1376*m*, 1336*s*, 1311*s*, 1277*s*, 1187*m*, 1108*m*, 1071*w*, 1046*m*, 1027*w*. ^{1}H-NMR (223 K; major isomer)[12]: 10.20 (s, NH); 8.03, 7.63 ($AA'BB'$, J = 8.5, 4 arom. H); 7.88 (s, H–C(5)); 7.19 (t-like, 2 arom. H); 7.08–6.98 (m, 2 arom. H); 6.94–6.82 (m, 3 arom. H); 6.78 (d-like, 2 arom. H). ^{13}C-NMR (223 K; major isomer): 162.4, 145.6 (2s, C(2), C(4)); 151.0 (s, CN_2); 147.1, 146.3, 140.4, 130.1 (4s, 4 arom. C); 129.9, 128.7, 128.1, 127.9, 126.1, 123.6, 123.1, 122.5 (8d, 14 arom. C); 117.3 (d, C(5)). CI-MS: 449 (100, $[M+1]^+$), 418 (30), 256 (21). Anal. calc. for $C_{22}H_{16}N_4O_2Se$ (447.36): C 59.06, H 3.58, N 12.53; found: C 58.91, H 3.63, N 12.50.

4-Chloro-N^2-*[4-(4-nitrophenyl)-1,3-selenazol-2-yl]*-N^1-*phenylbenzimidamide* (**10b**). From 2.5 mmol of **7l** and 4-nitrophenacyl bromide: 1.05 g (87%). M.p. 223–224° (EtOH). IR: 3384*m*, 3063*w*, 1644*s*, 1594*s*, 1542*s*, 1507*s*, 1450*m*, 1408*w*, 1342*s*, 1310*m*, 1296*m*, 1274*s*, 1184*w*, 1101*m*, 1088*m*, 1044*m*, 1016*m*. ^{1}H-NMR (major isomer)[13]: 10.30 (s, NH); 8.15, 7.84 ($AA'BB'$, J = 8.8, 4 arom. H); 7.92 (s, H–C(5)); 7.35–6.90 (m, 7 arom. H); 6.75 (d-like, 2 arom. H). ^{13}C-NMR (major isomer): 162.3, 146.4 (2s, C(2), C(4)); 150.6 (s, CN_2); 148.5, 146.3, 140.4, 138.5, 130.6 (5s, 5 arom. C); 129.5, 128.8, 128.6, 126.4, 123.8, 123.5, 122.4 (7d, 13 arom. C); 117.3 (d, C(5)). CI-MS: 483 (100, $[M+1]^+$), 453 (33), 370 (32), 231 (12). Anal. calc. for $C_{22}H_{15}ClN_4O_2Se$ (481.80): C 54.83, H 3.12, Cl 7.37, N 11.63; found: C 54.57, H 3.13, Cl 7.48, N 11.58.

6. *Isolation of Intermediate Isoselenoureas* **11**: *General Procedure* (*cf. Sect. 4*). To a stirred soln. of **7** in acetone, 1 equiv. of bromide ($BrCH_2Z$) was added at r.t. After a few min, the mixture was concentrated *i.v.*, and the precipitate was filtered. The solid was suspended in acetone, and 1 equiv. of Et_3N was added. After stirring for 10–30 min, the mixture was poured into ice/H_2O and stirred for another 10 min to 1 h. The precipitate was filtered by suction and air-dried. For anal. purposes, an aliquot was recrystallized to give white crystals.

Ethyl 2-{[((Morpholin-4-yl){[(phenyl)(phenylimino)methyl]imino})methyl]selanyl}acetate (**11a**). From 4.4 mmol of **7a** and ethyl 2-bromoacetate: 1.90 g (94%). M.p. 63.5–64° (Et_2O). IR: 3061*w*, 2956*m*, 2842*w*, 1731*s*, 1606*s*, 1579*s*, 1482*m*, 1447*m*, 1425*w*, 1410*w*, 1392*m*, 1365*m*, 1309*m*, 1285*m*, 1263*s*, 1226*m*, 1218*m*, 1193*w*, 1167*m*, 1111*s*, 1057*m*, 1016*s*, 1001*m*. ^{1}H-NMR: 8.00–7.96 (m, 2 arom. H); 7.46–7.37 (m, 3 arom. H); 7.30–7.25 (m, 2 arom. H); 7.01–6.96 (m, 3 arom. H); 4.01 (q, J = 7.1, MeCH_2O); 3.54 (t, J = 4.6, 2 CH_2O); 3.43 (t, J = 4.5, 2 CH_2N); 3.27 (s with satellite, J = 6.2, CH_2Se); 1.15 (t, J = 7.1, Me). ^{13}C-NMR: 169.4 (s, CO); 158.7, 150.0 (2s, $SeCN_2$, CN_2); 148.9, 136.4 (2s, 2 arom. C); 130.4, 128.3, 128.1, 122.7, 122.1 (5d, 10 arom. C); 66.3 (t, 2 CH_2O); 61.5 (t, MeCH_2O); 48.9 (t, 2 CH_2N); 27.2 (t, CH_2Se); 13.9 (q, Me). CI-MS: 460 (5, $[M+1]^+$), 367 (73), 294 (49), 94 (100). Anal. calc. for $C_{22}H_{25}N_3O_3Se$ (458.42): C 57.64, H 5.46, N 9.17; found: C 57.57, H 5.62, N 9.17.

N^1-*{[(Cyanomethyl)selanyl][(methyl)(phenyl)amino]methylidene}*-N^2-*phenylbenzimidamide* (**11b**). From 1.4 mmol of **7e** and 2-bromoacetonitrile: 0.56 g (95%). M.p. 105.5–106° (Et_2O). IR: 3059*w*, 2999*w*, 2932*w*, 2242*m*, 1618*s*, 1578*s*, 1560*s*, 1492*s*, 1480*s*, 1446*m*, 1414*s*, 1374*m*, 1347*s*, 1307*m*, 1272*s*, 1216*m*, 1185*w*, 1165*m*,

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[12]) There are signals for two isomers present (ratio *ca.* 3:1). The second isomer shows signals for NH at 12.70 and for the $AA'BB'$ system at 8.33, 7.94 ppm (J = 8.5).

[13]) There are signals for two isomers present (ratio *ca.* 3:2). The second isomer shows signals for NH at 12.65, for the $AA'BB'$ system at 8.28, 7.95 (J = 8.5), and for H–C(5) at 8.06 ppm.

1115*m*, 1068*m*, 1023*m*, 1008*w*. ^{1}H-NMR: 8.21–8.16 (*m*, 2 arom. H); 7.49–7.45 (*m*, 3 arom. H); 7.39 (*t*-like, 2 arom. H); 7.28–7.20 (*m*, 3 arom. H); 7.12 (*t*-like, 1 arom. H); 7.05 (*d*-like, 2 arom. H); 6.58 (*dd*, 2 arom. H); 3.35 (*s* with satellite, $J = 8.2$, CH_2Se); 3.13 (*s*, MeN). ^{13}C-NMR: 157.2, 150.0 (2*s*, $SeCN_2$, CN_2); 148.8, 142.6, 136.3 (3*s*, 3 arom. C); 130.8, 129.4, 128.9, 128.7, 128.4, 128.2, 127.9, 122.8, 121.9 (9*d*, 15 arom. C); 117.4 (*s*, C≡N); 41.3 (*q*, MeN); 8.7 (*t*, CH_2Se). CI-MS: 431 (<1, $[M+1]^+$), 340 (100), 94 (67). Anal. calc. for $C_{23}H_{20}N_4Se$ (431.40): C 64.04, H 4.64, N 12.99; found: C 63.92, H 4.74, N 12.98.

N^1-*[[(4-Cyanobenzyl)selanyl][(methyl)(phenyl)amino]methylidene]-4-methyl*-N^2-*phenylbenzimidamide* (**11c**). From 6.8 mmol of **7i** and 4-(bromomethyl)benzonitrile: 3.25 g (92%). M.p. 124–124.5° (Et_2O). IR: 3059*w*, 3027*w*, 2925*w*, 2227*m*, 1621*s*, 1591*s*, 1574*s*, 1552*s*, 1507*m*, 1493*m*, 1446*w*, 1416*m*, 1342*m*, 1307*w*, 1269*m*, 1258*m*, 1214*m*, 1189*w*, 1174*m*, 1116*m*, 1068*w*, 1019*w*, 1001*w*. ^{1}H-NMR: 7.91 (*AA′* of *AA′BB′*, $J = 8.2$, 2 arom. H); 7.42 (*AA′* of *AA′BB′*, $J = 8.3$, 2 arom. H); 7.33 (*t*-like, 2 arom. H); 7.24–7.20 (*m*, 5 arom. H); 7.15–7.03 (*m*, 5 arom. H); 6.71–6.65 (*m*, 2 arom. H); 3.48 (*s*, CH_2Se); 3.18 (*s*, MeN); 2.43 (*s*, Me). ^{13}C-NMR: 157.8, 150.3 (2*s*, $SeCN_2$, CN_2); 144.0, 143.8, 140.8, 134.0, 110.5 (5*s*, 6 arom. C); 132.0, 129.7, 129.1, 128.8, 128.6, 128.1, 127.8, 127.7, 122.5, 122.2 (10*d*, 18 arom. C); 118.6 (*s*, C≡N); 41.2 (*q*, MeN); 31.4 (*t*, CH_2Se); 21.4 (*q*, Me). Anal. calc. for $C_{30}H_{26}N_4Se$ (521.53): C 69.10, H 4.99, N 10.75; found: C 68.83, H 5.07, N 10.67.

N^1-*{[(4-Cyanobenzyl)selanyl](morpholin-4-yl)methylidene}-4-methyl*-N^2-*phenylbenzimidamide* (**11d**). From 2.5 mmol of **7f** and 4-(bromomethyl)benzonitrile: 1.19 g (94%). M.p. 220–221° (acetone). IR: 3052*w*, 3025*w*, 2964*w*, 2921*w*, 2849*w*, 2224*m*, 1609*s*, 1595*s*, 1580*s*, 1507*w*, 1482*m*, 1461*w*, 1443*w*, 1424*w*, 1411*w*, 1394*m*, 1308*w*, 1292*m*, 1266*m*, 1225*w*, 1189*w*, 1199*m*, 1189*m*, 1169*m*, 1106*m*, 1068*m*, 1021*m*, 1014*m*, 1002*m*. ^{1}H-NMR: 7.71 (*AA′* of *AA′BB′*, $J = 8.2$, 2 arom. H); 7.40 (*AA′* of *AA′BB′*, $J = 8.3$, 2 arom. H); 7.28–7.24 (*m*, 2 arom. H); 7.17 (*BB′* of *AA′BB′*, $J = 8.1$, 2 arom. H); 7.08 (*BB′* of *AA′BB′*, $J = 8.2$, 2 arom. H); 7.00–6.96 (*m*, 3 arom. H); 3.80 (*s* with satellite, $J = 6.3$, CH_2Se); 3.51 (*t*, $J = 4.6$, 2 CH_2O); 3.44 (*t*, $J = 4.6$, 2 CH_2N); 2.42 (*s*, Me). ^{13}C-NMR: 159.0, 150.1, (2*s*, $SeCN_2$, CN_2); 148.3, 143.5, 140.7, 133.9, 110.8 (5*s*, 5 arom. C); 132.1, 129.4, 128.8, 128.4, 127.9, 122.6, 122.3 (7*d*, 13 arom. C); 118.5 (*s*, C≡N); 66.3 (*t*, 2 CH_2O); 48.9 (*t*, 2 CH_2N); 30.7 (*t*, CH_2Se); 21.4 (*q*, Me). CI-MS: 503 (100, $[M+1]^+$), 388 (90), 308 (81). Anal. calc. for $C_{27}H_{26}N_4OSe$ (501.49): C 64.67, H 5.19, N 11.18; found: C 64.57, H 5.36, N 11.21.

Ethyl 2-[({[(4-chlorophenyl)(phenylimino)methyl]imino}(morpholin-4-yl)methyl)selanyl]acetate (**11e**). From 5.05 mmol of **7j** and ethyl 2-bromoacetate: 2.17 g (87%). M.p. 108.5–109° (Et_2O). IR: 2957*m*, 2922*w*, 2848*w*, 1730*s*, 1606*s*, 1576*s*, 1487*m*, 1444*m*, 1425*w*, 1395*m*, 1365*w*, 1301*m*, 1287*m*, 1263*s*, 1194*m*, 1163*m*, 1112*s*, 1092*m*, 1057*m*, 1018*s*, 1012*s*, 1001*m*. ^{1}H-NMR: 7.93, 7.38 (*AA′BB′*, $J = 8.7$, 4 arom. H); 7.30–7.23 (*m*, 2 arom. H); 7.02–6.95 (*m*, 3 arom. H); 4.02 (*q*, $J = 7.1$, Me*CH*$_2$O); 3.54 (*t*, $J = 4.6$, 2 CH_2O); 3.43 (*t*, $J = 4.5$, 2 CH_2N); 3.25 (*s* with satellite, $J = 6.3$, CH_2Se); 1.16 (*t*, $J = 7.1$, Me). ^{13}C-NMR: 169.3 (*s*, CO); 157.6, 149.7 (2*s*, $SeCN_2$, CN_2); 149.3, 136.5, 135.0 (3*s*, 3 arom. C); 129.4, 128.3, 128.2, 122.8, 122.1 (5*d*, 9 arom. C); 66.3 (*t*, 2 CH_2O); 61.6 (*t*, Me*CH*$_2$O); 48.9 (*t*, 2 CH_2N); 27.2 (*t*, CH_2Se); 13.9 (*q*, Me). CI-MS: 494 (28, $[M+1]^+$), 401 (34), 328 (51), 94 (100). Anal. calc. for $C_{22}H_{24}ClN_3O_3Se$ (492.87): C 53.61, H 4.90, Cl 7.19, N 8.53; found: C 53.41, H 5.02, Cl 7.35, N 8.53.

N^1-*[[(Cyanoethyl)selanyl][(methyl)(phenyl)amino]methylidene]-4-methyl*-N^2-*phenylbenzimidamide* (**11f**). From 1.5 mmol of **7i** and 3-bromopropionitrile: 0.59 g (85%). M.p. 144.2–144.5° (Et_2O). IR: 3064*w*, 2995*w*, 2934*w*, 2253*w*, 1601*s*, 1587*s*, 1556*s*, 1508*m*, 1492*s*, 1446*m*, 1412*m*, 1340*m*, 1306*w*, 1286*w*, 1257*s*, 1210*m*, 1187*w*, 1169*m*, 1116*m*, 1074*w*, 1023*m*. ^{1}H-NMR: 7.96 (*d*-like, 2 arom. H); 7.35 (*t*-like, 2 arom. H); 7.29–7.22 (*m*, 5 arom. H); 7.12–7.03 (*m*, 3 arom. H); 6.74–6.71 (*m*, 2 arom. H); 3.17 (*s*, MeN); 2.78, 2.51 (2*t*, 2 CH_2); 2.42 (*s*, Me). ^{13}C-NMR: 157.7, 150.3 (2*s*, $SeCN_2$, CN_2); 150.0, 143.8, 140.9, 133.9 (4*s*, 4 arom. C); 129.2, 129.0, 128.7, 128.1, 127.8, 122.6, 122.0 (7*d*, 14 arom. C); 118.6 (*s*, C≡N); 41.2 (*q*, MeN); 22.3, 18.7 (2*t*, 2 CH_2); 21.4 (*q*, Me). CI-MS: 461 (100, $[M+1]^+$), 406 (13), 343 (17), 328 (50). Anal. calc. for $C_{25}H_{24}N_4Se$ (459.46): C 65.36, H 5.23, N 12.20; found: C 65.29, H 5.40, N 12.08.

7. *Preparation of 1,3-Selenazoles* **12**. To a soln. of an ethyl 1,3-selenazole-5-carboxylate in acetone, an aq. soln. of NaOH (5%) was added (2–3 equiv. of NaOH). Then, acetone was added to obtain a homogenous soln., and the mixture was heated under reflux. After 2 h, the starting material was consumed (TLC), the mixture was poured into ice/H_2O, and the product was isolated by filtration.

4-[4-(4-Methylphenyl)-1,3-selenazol-2-yl]morpholine (**12a**). From 2.5 mmol of **9l**: 0.54 g (71%). M.p. 82.5–83.5°. IR: 3100*w*, 3031*w*, 2977*w*, 2921*m*, 2871*m*, 2839*m*, 1538*s*, 1489*m*, 1447*m*, 1434*m*, 1371*m*, 1319*m*, 1297*m*, 1278*m*, 1225*s*, 1197*w*, 1177*m*, 1114*s*, 1074*w*, 1043*m*, 1021*m*. ^{1}H-NMR: 7.72, 7.15 (*AA′BB′*, $J = 4$ arom. H); 7.29 (*s* with satellite, $J = 25.7$, H–C(5)); 3.81 (*t*, $J = 4.9$, 2 CH_2O); 3.52 (*t*, $J = 4.9$, 2 CH_2N); 2.34 (*s*, Me). ^{13}C-NMR: 172.9, 152.8 (2*s*, C(2), C(4)); 137.1, 133.0 (2*s*, 2 arom. C); 129.1, 126.2 (2*d*, 4 arom. C); 105.0 (*d*, C(5)); 66.2 (*t*, 2 CH_2O); 49.6 (*t*, 2 CH_2N); 21.1 (*q*, Me). CI-MS: 309 (100, $[M+1]^+$), 290 (20), 94 (27). Anal. calc. for $C_{14}H_{16}N_2OSe$ (307.26): C 54.72, H 5.21, N 9.12; found: C 54.94, H 5.20, N 9.18.

4-(4-Chlorophenyl)-N-*methyl*-N-*phenyl-1,3-selenazol-2-amine* (**12b**). From 3.8 mmol of **9s**: 1.01 g (76%). M.p. 137.7–139° (Et_2O). IR: 3078*w*, 2988*w*, 2905*w*, 2886*w*, 1594*w*, 1582*m*, 1529*s*, 1500*s*, 1474*s*, 1397*m*, 1338*m*, 1318*m*, 1306*m*, 1286*m*, 1253*s*, 1174*m*, 1126*w*, 1083*m*, 1050*m*, 1032*m*, 1009*m*. ^{1}H-NMR: 7.80, 7.31 ($AA'BB'$, J = 8.7, 4 arom. H); 7.45–7.41 (*m*, 4 arom. H); 7.32–7.25 (*m*, 1 arom. H); 7.18 (*s* with satellite, J = 24.6, H–C(5)); 3.59 (*q*, MeN). ^{13}C-NMR: 171.6, 151.4 (2*s*, C(2), C(4)); 147.3, 134.4, 132.8 (3*s*, 3 arom. C); 129.9, 128.5, 127.5, 126.8, 125.1 (5*d*, 9 arom. C); 106.0 (*d*, C(5)); 40.3 (*q*, MeN). CI-MS: 349 ($[M+1]^+$). Anal. calc. for $C_{16}H_{13}ClN_2Se$ (347.70): C 55.27, H 3.77, Cl 10.20, N 8.06; found: C 55.27, H 3.83, Cl 10.40, N 8.05.

8. *Crystal-Structure Determination of* **7f**, **9c**, *and* **9d** (see *Table 4*, and *Figs. 1* and *3*)[14]). All measurements were performed on a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction based on ψ scans was applied in the cases of **7f** and **9d** [37], whereas, in the case of **9c**, an empirical absorption correction by means of the program DIFABS [38] was applied. Data collection and refinement parameters are given in *Table 4*, views of the molecules are shown in *Figs. 1* and *3*. The structures were solved by direct methods

Table 4. *Crystallographic Data of Compounds* **7f**, **9c**, *and* **9d**

	7f	**9c**	**9d**
Crystallized from	acetone	EtOH	acetone
Empirical formula	$C_{19}H_{21}N_3OSe$	$C_{23}H_{17}N_3O_3Se$	$C_{22}H_{22}N_2O_2Se$
Formula weight [g mol^{-1}]	386.29	462.30	425.33
Crystal color, habit	yellow, prism	yellow, irregular prism	pale yellow, prism
Crystal dimensions [mm]	0.17 × 0.40 × 0.43	0.20 × 0.33 × 0.45	0.25 × 0.32 × 0.40
Temperature [K]	173(1)	173(1)	173(1)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4
Reflections for cell determination	25	25	25
2θ Range for cell determination [°]	39–40	24–26	39–40
Unit-cell parameters a [Å]	8.982(3)	12.594(1)	10.229(5)
b [Å]	13.577(4)	14.834(3)	9.765(4)
c [Å]	14.726(2)	10.986(2)	19.784(4)
β [°]	104.24(2)	102.26(1)	103.30(3)
V [Å^3]	1740.5(7)	2005.5(6)	1923(1)
D_x [g cm^{-3}]	1.474	1.531	1.469
μ(MoK_α) [mm^{-1}]	2.167	1.902	1.971
$2\theta_{(max)}$ [°]	55	55	55
Transmission factors (min; max)	0.491; 0.692	0.485; 0.683	0.511; 0.611
Total reflections measured	4434	5026	4934
Symmetry-independent reflections	4003	4604	4417
Reflections used [$I > 2\sigma(I)$]	2996	3148	3296
Parameters refined	302	340	333
Final R	0.0345	0.0445	0.0332
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$	0.0282	0.0388	0.0278
Goodness of fit	1.460	1.920	1.434
Secondary extinction coefficient	$1.6(4) \times 10^{-7}$	$6(5) \times 10^{-8}$	$3.7(3) \times 10^{-7}$
Final Δ_{max}/σ	0.001	0.0004	0.0006
$\Delta\rho$ (max; min) [e Å^{-3}]	0.39; −0.48	0.66; −0.55	0.39; −0.38

[14]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications No. CCDC-141338–141340 for **7b**, **9c**, and **9d**, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

using SIR92 [39], which revealed the position of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were located in difference electron-density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. Refinement of each structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_c|)^2$. A correction for secondary extinction was applied. Neutral-atom scattering factors for non-H-atoms were taken from [40a] and the scattering factors for H-atoms from [41]. Anomalous dispersion effects were included in F_c [42]; the values for f' and f'' were those of [40b], and the values of the mass-attenuation coefficients were those of [40c]. All calculations were performed using the *teXsan* crystallographic software package [43].

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