2-(3-ACYLSELENOUREIDO)BENZONITRILES AND 2-(3-ACYLSELENOUREIDO)THIOPHENE-3-CARBONITRILES. PREPARATION, STRUCTURE ELUCIDATION, CYCLIZATION AND RETROCYCLIZATION REACTIONS

Jiří Šibor[a1], Dalimil Žůrek[a], Radek Marek[a2], Michal Kutý[a3], Otakar Humpa[a4], Jaromír Marek[b1] and Pavel Pazdera[a5,*]

[a] *Department of Organic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic; e-mail: [1] sibor@chemi.muni.cz, [2] rmarek@chemi.muni.cz, [3] michal@chemi.muni.cz, [4] humpa@chemi.muni.cz, [5] pazdera@chemi.muni.cz*

[b] *Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic; e-mail: marek@chemi.muni.cz*

Received January 25, 1999
Accepted June 8, 1999

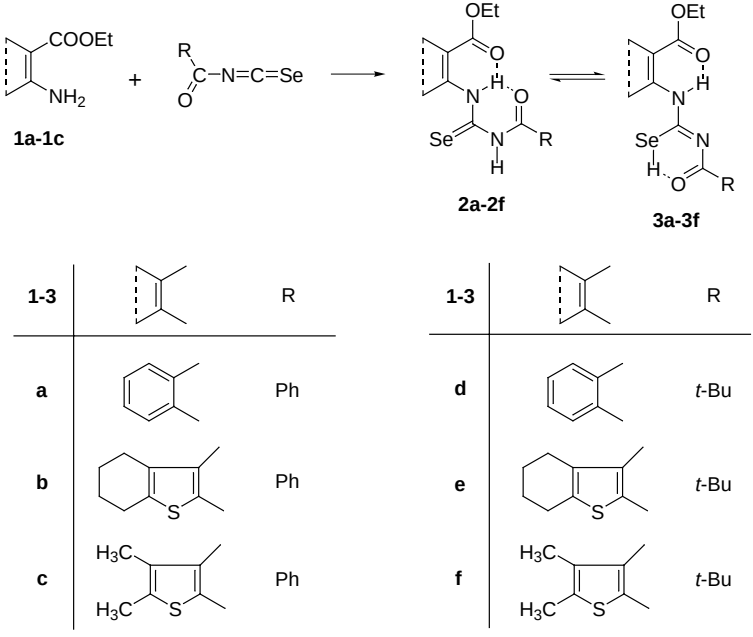
Dedicated to Professor Otto Exner on the occasion of his 75th birthday.

Synthesis of 2-(3-acylselenoureido)benzonitriles and 2-(3-acylselenoureido)thiophene-3-carbonitriles **5a**–**5f** by addition of 2-aminonitriles **4a**–**4c** to benzoyl- or 2,2-dimethylpropanoylisoselenocyanate and their cycloaddition reactions are described. Structures of compounds **5a**–**5f** were supported by CIMS, FTIR, ^{1}H, ^{13}C, ^{77}Se and ^{15}N NMR spectra. The parameters of ^{15}N and ^{77}Se nuclei were obtained from inverse ^{1}H-X 2D HMBC and GSQMBC correlation experiments at natural abundance. Structure of compound **5b** was confirmed by X-ray analysis. The geometry of **5b** was optimized by *ab initio* RHF/DZVP quantum chemistry calculation. A very good correlation between the calculation and experimental data was found. The geometry of **5e** was optimized by *ab initio* DFT/VWN/DZVP quantum chemistry calculation. It was found that title compounds **5a**–**5f** do not undergo isomerization to acylisoselenoureas, in contrast to analogous ester derivatives. Fused 6-imino-6*H*-1,3-selenazinium salts (chlorides **6a**–**6f**, hydrogensulfates **7a**–**7f** and tetrafluoroborates **8a**–**8f**) were prepared by an acid cyclization of **5a**–**5f**. It was found that neutralization of **6a**–**6f**, **7a**–**7f** and **8a**–**8f** led to their retrocyclization to **5a**–**5f**. Selenoureas **5a**–**5f** with equimolar amounts of methanolic potassium hydroxide afforded potassium salts **9a**–**9f**. Only the salts **9b**, **9c**, **9e** and **9f** of the thiophene series were isolated. Their heating in methanol solution led to deacylation of isoselenoureas **10b** and **10c**. The *in situ* prepared compounds **9a** and **9d** cyclized and deacylated to 4-aminoquinazoline-2-selenole **11a** under the same conditions. The compounds **5a**–**5f** and **10a**–**10c** cyclized to fused 4-aminopyrimidine-2-selenols **11a**, **11b** and 4-aminopyrimidine-2-selenone **12c** by boiling in methanolic potassium hydroxide solution.

Key words: Acylselenoureas; Fused 1,3-selenazines; Fused pyrimidines; 2-Aminothiophene-3-carbonitriles; 2-Aminobenzonitrile; NMR spectroscopy, multinuclear; *Ab initio* calculations; X-Ray diffraction; Selenium heterocycles.

The interest of our research group in the past few years has been focused on the synthesis of fused 1,3-thiazines, pyrimidines, 1,3-selenazines and 1,3-oxazines. The precursors available for their synthesis are functional derivatives of carbonic acid (ureas, thioureas, selenoureas or guanidines) derived from 2-amino substituted aromatic or heteroaromatic nitriles or esters. These precursors cyclize to the corresponding azine skeletons under acid or base catalysis.

In the literature the syntheses of the title cyano substituted acylselenoureas have not been described yet. However, we published the synthesis[1] of analogous ethyl esters **2a**–**2f** and their isomerization to acylisoselenoureas **3a**–**3f** initiated photochemically, thermally or by the action of acid (Scheme 1).



1-3		R
a		Ph
b		Ph
c	H_3C, H_3C	Ph

1-3		R
d		*t*-Bu
e		*t*-Bu
f	H_3C, H_3C	*t*-Bu

SCHEME 1

Structure of both types of isomers was supported by FTIR, ^{1}H, ^{13}C, ^{15}N and ^{77}Se NMR spectroscopies. The results from spectral study were supported by X-ray structural analysis and also by *ab initio* quantum chemistry calculations.

Ester analogues[1] **2a**–**2f** of title compounds were synthesized by addition of 2-aminoesters **1a**–**1c** to carbon atom of isoselenocyanato group in

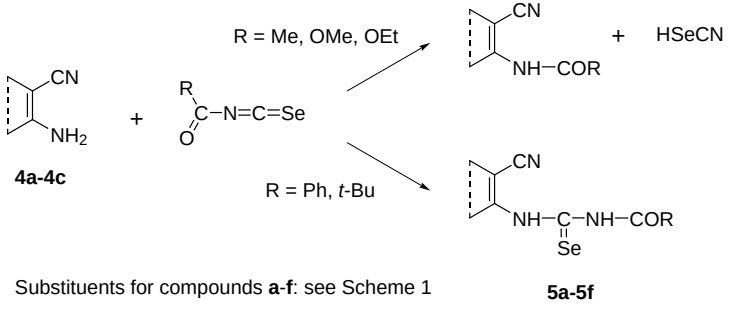
benzoyl- and 2,2-dimethylpropanoylisoselenocyanate, respectively. The reactions were carried out in acetone solution at room temperature. An attempt to prepare analogous acetyl- and (alkoxycarbonyl)selenoureas was unsuccessful. Nor was successful the acylation of starting amines by acylisoselenocyanates. Instead, competitive attack of the amino group on the acyl carbon atom appeared.

Similar isomerization has not been observed with the title cyano compounds. However, cyclization reactions of sulfur analogues of title compounds in basic[2–8] and acid[8–12] medium were studied at full length. The reactivity of ureido analogues was studied as well[13,14].

The goal of this work was preparation of the title acylselenoureas and study of their reactivity in acid-initiated cycloaddition giving fused 1,3-selenazines, cyclization by the action of the bases leading to fused 1,2-dihydropyrimidine-2-selenones, as well as their retrocyclization reactions.

RESULTS AND DISCUSSION

We have attempted to prepare (acylselenoureido)nitriles **5a**–**5f** by an addition of corresponding amines **4a**–**4c** to acylisoselenocyanates (Scheme 2) analogously to the synthesis[1] of (acylselenoureido)esters **2a**–**2f**. Acetyl-, benzoyl-, 2,2-dimethylpropanoyl-, ethoxycarbonyl- and methoxycarbonylisoselenocyanate prepared *in situ* were used in their acetone solutions. In accordance with the results obtained with ester analogues, we have ob-



SCHEME 2

tained good yields only with benzoyl- and 2,2-dimethylpropanoylisoselenocyanates. The other acylisoselenocyanates gave either the acylation product of the starting aminoester (identified by comparison with the product obtained by acylation of the corresponding amines with acyl chlorides) or a mixture of this compounds with acylselenourea. The same results were described earlier for analogous addition reactions[1,15–18].

Benzoylselenoureas **5a**–**5c** were also synthesized by the reaction of benzoylisoselenocyanate oligomer with starting amines **4a**–**4c** in boiling toluene solution. The yields of **5a**–**5c** were about 10–15% lower than with benzoylisoselenocyanate monomer generated *in situ*.

Identification of acylselenoureas **5a**–**5f** was based on C, H, N and Se elemental analysis, mass spectroscopy, FTIR spectra and ^{1}H, ^{13}C, ^{77}Se and ^{15}N NMR spectroscopy. The spectral data were compared with the data found for ester analogues and a good correlation between their spectral parameters was found.

In mass spectra, molecular peak M^+, peak $(M + 1)^+$, and fragments of $(RCO)^+$, $(HNCSe)^+$, $(M - RCO)^+$, $(M - SeH)^+$, $(M - HseCN)^+$ and $(NHCSeNHCOR)^+$ were found. A similar fragmentation was observed in the case of the sulfur analogues and products of their acid cyclization, *i.e.* 1,3-thiazinium salts[8–10].

In FTIR spectra of compounds **5a**–**5f**, the band of cyano group, the corresponding bands of –NHCO– group (amide I and amide II bands)[19] and selenoureido group (selenoamide I and III bands)[20] as well as stretching vibration bands of N–H were found.

^{1}H NMR spectroscopy of compounds **5a**–**5f** confirms the presence of protons localized on the basic skeletons, acyl groups and both nitrogen atoms of the selenoureido group. Proton signals of the NHCSe groups are significantly deshielded, compared with NHCO, similarly to the ester analogues, due to the hydrogen bonding effects. The signal of NHCSe proton in nitriles **5a**–**5f** is shifted approximately 0.5 ppm upfield in comparison with the ester analogues, probably because of a different electron-withdrawing behaviour of the cyano and ethoxycarbonyl groups. The comparison of the chemical shifts at the NHCSe group proton in the benzoyl and 2,2-dimethylpropanoyl series indicates stronger interaction of the NHCSe group proton with acyl oxygen atom in the former compounds.

Assignment of the proton signals was carried out on the basis of 2D chemical shift correlation experiments for selected compounds **5a**–**5f**. The signals for other compounds were assigned on the basic of analogy. ^{1}H–^{1}H dipolar interactions for compounds **5a**–**5f** were determined by 2D NOESY experiment. For observation of heteronuclear ^{1}H–^{13}C interactions (both direct and long-range) HETCOR, COLOC, HSQC and HMBC pulse sequences were used. The single-bond ^{13}C-^{77}Se coupling constants were extracted from the ^{77}Se satelites observed in ^{13}C (^{1}H) spectra. HMBC and GSQMBC experiments were also used for detection of ^{1}H–^{5}N and ^{1}H–^{77}Se long-range interactions. The detailed NMR study on heteronuclear long-range coupling constants will be presented elsewhere[21].

A single crystal of 2-(3-benzoylselenoureido)-4,5,6,7-tetrahydrobenzo-[1]thiophene-3-carbonitrile hemihydrate (**5b**) was used for the X-ray structural analysis. The sample suitable for X-ray study was obtained by crystallization from chloroform saturated at room temperature with water and then with compound **5b**. The crystallization was carried out in a 5 mm NMR tube at –30 °C. Preparation of a suitable single crystal of anhydrous compound **5b** was unsuccessful because the crystals developed only in one dimension as long needles and provided diffraction insufficient for analysis. The found structural data presented in Tables I–III correspond very well with those calculated by *ab initio* DSF quantum chemistry calculations. Both the calculated and X-ray molecular structures of **5b** are presented in Figs 1 and 2. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-116 933. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk. Since we could not obtain suitable single crystals of **5e** and the reported correspondence between the X-ray and *ab initio* RHF data for compound **5b** was very good, we tried to model and optimize the molecular structure of 2,2-dimethylpropanoyl analogues **5e** by DFT/VWN/DZVP quantum chemistry method. The molecular design of compound **5e** is presented in Fig. 3 and some structural data in Tables I–III. The obtained results showed that the hydrogen bond between the NHCSe hydrogen and the carbonyl oxygen is stronger in the case of benzoyl derivative than in its 2,2-dimethylpropanoyl analogue. This observation is in good accord with the ^{1}H NMR spectra.

The ester analogues of title compounds underwent isomerization to acylisoselenoureas[1]. In the case of nitriles **5a**–**5f**, the isomerization initiated by light or controlled heating was unsuccessful. The attempted

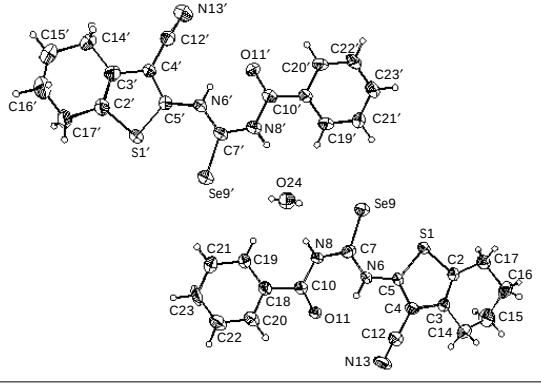


FIG. 1
Molecular structure of **5b** according to the X-ray analysis

isomerization of **5a**–**5f** by boiling in acetic acid led to the corresponding 1,3-selenazinium acetates. These were separated from the reaction mixture as tetrafluoroborates **8a**–**8f**. The formation of the corresponding 1,3-selenazinium chlorides using hydrogen chloride in anhydrous methanol was also observed.

Higher thermodynamic stability of isoselenoureas is probably the reason for the isomerization in ester series. However, the nitriles are more stable than selenoureas. Thermal analysis also showed an exothermic process[1] during isomerization of ester analogues. In the case of nitriles **5a**–**5f**, this process was not observed. The stability of both isomers is dependent on two types of intramolecular hydrogen bonds. This fact was shown by the NMR studies and *ab initio* quantum chemistry calculations[1]. The first hydrogen bond exists between the carbonyl oxygen atom of the ester function and the NHCSe group hydrogen atom; the other type is formed between the acyl oxygen atom and Se–H hydrogen atom. These hydrogen bonds do not exist in nitrile series (Figs 1–3). On the other hand, compounds **5a**–**5f**

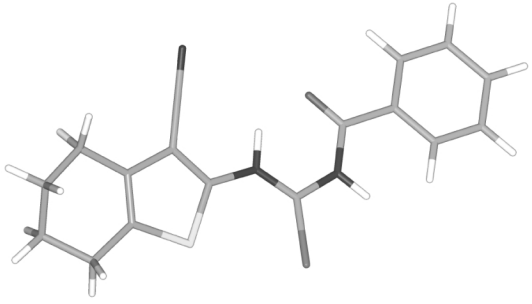


FIG. 2
Molecular design of **5b** according to the computational chemistry

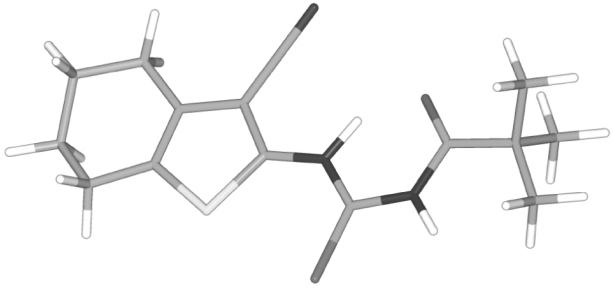


FIG. 3
Molecular design of **5e** according to the computational chemistry

TABLE I
Selected interatomic distances (Å) in **5b** and **5e**

Bond	**5b** (X-ray)	**5b** (calculated)	**5e** (calculated)
C5–N6	1.39	1.39	1.38
N6–C7	1.33	1.33	1.33
C5–N6	1.37	1.36	1.36
N6–C7	1.38	1.38	1.38
C10–C18	1.50	1.49	1.30
C7–Se9	1.81	1.83	1.81
N6–NH6	0.86	1.02	1.15
N8–NH8	0.86	1.04	1.02
C10–O11	1.21	1.22	1.23
S1–C5	1.72	1.72	1.72
C4–C5	1.37	1.38	1.38
C4–C12	1.43	1.44	1.44
C12–N13	1.13	1.17	1.15

TABLE II
Selected valency angles (°) in **5b** and **5e**

Angle	**5b** (X-ray)	**5b** (calculated)	**5e** (calculated)
C5–N6–NH6	114.56	115.05	115.26
NH6–N6–C7	114.95	114.82	114.84
C5–N6–C7	130.49	131.27	132.85
N6–C7–N8	115.89	116.17	116.26
N6–C7–Se9	125.51	127.09	124.35
Se9–C7–N8	118.60	119.06	119.47
C7–N8–C10	127.18	128.74	128.04
N8–C10–C18	117.19	117.35	117.17
O11–C10–C18	121.60	123.26	123.27
O11–C10–N8	121.20	122.85	124.15
C5–C4–C12	123.24	124.84	122.36
C4–C12–N13	177.67	178.26	179.28

show the hydrogen bond between the acyl oxygen atom and the NHCSe group hydrogen, which is shorter and stronger. Table IV contains hydrogen bond distances of both selenourea types and isoselenoureas for the 4,5,6,7-tetrahydrobenzo[1]thiophene skeleton as a model.

It is well known[8–12] that in the acidic medium, the sulfur analogues of title compounds **5a**–**5f** may cyclize by an attack of the sulfur on the nitrile carbon to form the corresponding 1,3-thiazinium compound. These reactions proceeded in concentrated sulfuric acid at room temperature. When

TABLE III
Selected torsion angles (°) in **5b** and **5e**

Angle	**5b** (X-ray)	**5b** (calculated)	**5e** (calculated)
S1–C5–N6–NH6	179.73	184.35	181.42
NH6–N6–C7–Se9	–179.40	–179.79	–179.35
Se9–C7–N8–C10	172.00	171.45	176.15
C7–N8–C10–O11	3.75	4.15	3.71
C7–N8–C10–C18	–175.46	–0.86	–174.86
C5–N6–C7–N8	–179.81	–181.63	–180.06
N6–C5–C4–C12	1.67	1.78	1.74
S1–C5–C4–C12	–177.50	–178.24	–177.50

TABLE IV
Hydrogen bond lengths (Å) in the 4,5,6,7-tetrahydrobenzo[1]thiophene skeleton

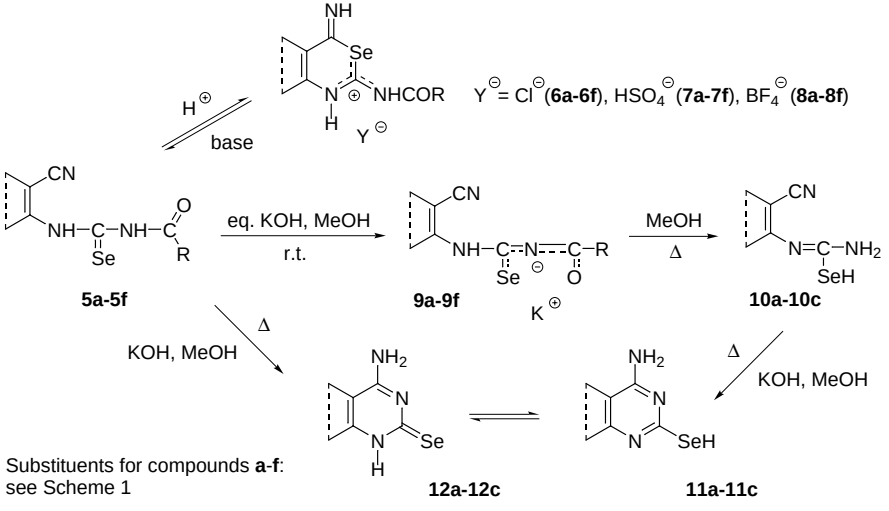
Compound	Hydrogen bond (X-ray/calculated)		
	N6H–O=C(acyl)	N6H–O=C(ester)	SeH–O=C(acyl)
5b	2.56/2.52	–	–
5e	–/2.63	–	–
2b[a]	–/2.72	–/1.96	–
2e[a]	2.87/2.84	1.95/1.93	–
3b[a]	–	–/2.72	–/2.89
3e[a]	–	–/2.63	–/2.99

the reaction was run at higher temperatures, the cyclization was followed by deacylation. In the reaction of the thiophene substrates, the corresponding 1,3-thiazines were not isolated after neutralization of reaction mixtures; instead, starting acylthioureas were obtained. It was found that in the neutral medium a retrocyclization reaction leading to the thiazinium ring opening occurred. Therefore, 2-acylamino-4-imino-4*H*-thieno[2,3-*d*]-[1,3]thiazinium salts were separated as lower soluble perchlorates[10,12].

Benzo-fused 2-acylamino-4-imino-4*H*-benzo[3,1]thiazines, prepared under the same conditions from corresponding acylthioureas in the benzonitrile series, are stable as free bases[11]. This fact is explained by a higher strain in the thiazine skeleton as a consequence of larger external bond angles of the thiophene ring[22].

In order to compare properties and reactivies of the 1,3-thiazine and 1,3-selenazine skeleton, 1,3-selenazinium hydrogensulfates **7a**–**7f** were prepared by cyclization of acylselenoureas **5a**–**5f** in concentrated sulfuric acid at room temperature (Scheme 3). We have observed that title selenoureas cyclized more rapidly in comparison with their sulfur analogues. The results of kinetic study of acid cyclization of title compounds, their sulfur and oxygen analogues and their comparison will be published later[13,14].

Hydrogensulfates **7a**–**7f** were soluble in water and polar solvents, though less than hydrogensulfates of analogous 1,3-thiazines. The low solubility and low stability of the prepared hydrogensulfates were observed also in hexadeuterodimethyl sulfoxide in the NMR measurements. Therefore, we have converted these salts to tetrafluoroborates **8a**–**8f** (Scheme 3).



SCHEME 3

Chlorides **6a**–**6f** were prepared by the cyclization of **5a**–**5f** in methanolic solution of hydrogen chloride (Scheme 3). For the above-presented reasons, we have attempted deacylation of **6a**–**6f** by the action of hydrogen chloride in methanolic solution at reflux but only destruction of these compounds was observed. Selane was eliminated and oxidized by the air oxygen to red modification of selenium. Selane was identified by the test with saturated solution of silver nitrate in vapors over the reaction mixture.

During the neutralization of 1,3-selenazinium salts **6a**–**6f**, **7a**–**7f** and **8a**–**8f** in aqueous solution with bases (ammonia, sodium hydroxide, sodium carbonate, sodium hydrogencarbonate and potassium analogues), respectively, the retrocyclization reaction to starting acylselenoureas **5a**–**5f** proceeded. In contrast to sulfur analogues, the retrocyclization was observed also with benzo[3,1]selenazinium derivatives **6a**, **6d**, **7a**, **7d**, **8a** and **8d**.

Identification of salts **6a**–**6f**, **7a**–**7f** and **8a**–**8f** was supported by the C, H, N, Se elemental analysis, mass spectroscopy (compounds **6b** and **7d**), FTIR, ^{1}H and ^{13}C NMR spectra and by comparison of the spectral data with those of the sulfur analogues[10,12]. Observed chemical shifts showed for the same 1,3-selenazinium salts with different anion and solvent in ^{1}H and ^{13}C NMR very good accordance. Assignment of the carbon signals based on correlation with the same values obtained by simulation.

Mass spectroscopy of **6b** and **7d** showed that the compounds during ionization eliminated hydrogen chloride and sulfuric acid, respectively. The behaviour of 1,3-thiazinium salts is analogous to that described previously[8].

In the FTIR spectra of salts **6a**–**6f**, **7a**–**7f** and **8a**–**8f** a broad band of the stretching N–H vibration and amide bands I–III (NHCO) were found. On the other hand, in the FTIR spectra, the stretching (N^+–H) vibration in the range 2 500–2 300 cm^{-1} was not observed. This demonstrates the fact that the selenazinium cation prefers one hydrogen atom on the ring N atom and one on the nitrogen atom of the acylamino group, the positive charge being delocalized around C2. As a consequence, the vibrational band of the (N–C^+(Se)–N) group of selenazinium cation was observed (see Scheme 3). In some cases, however, it was overlapped by the amide I band of the acylamino group.

Due to mentioned low solubility and stability of salts **6a**–**6f**, **7a**–**7f** and **8a**–**8f** in hexadeuterodimethyl sulfoxide, NMR spectra of chlorides **6a**–**6f** were measured in deuterotrifluoroacetic acid. ^{13}C NMR spectra supported the conclusion that the formal positive charge on the C2 atom of the selenazinium skeleton is delocalized. The value of C2 chemical shift is similar to that of the carbon atom in the isoselenoureido group of

electroneutral acylisoselenourea molecules[1]. The bonds C2–N1 and C2–Se are shorther as consequences of positive charge delocalization in the selenazine cation. Similar situation is in stable guanidinium cations. In the case of salts **6a**–**6f**, **7a**–**7f** and **8a**–**8f**, an involvement of electron density of the selenium atom to the π-system of selenazinium skeleton is probably predominant. The implication of this is a decrease in total energy of molecule caused by a decrease in internal tension of the selenazine ring. We have assumed that the increase in internal tension of skeleton in molecules **6a**–**6f**, **7a**–**7f** and **8a**–**8f** is caused by the size of selenium atom. This is larger in comparison with the nitrogen atom in 2-acylamino-4-imino-3,4-dihydroquinazolines[23] and their thiophene analogues[24]. The mentioned assumption may be supported by the fact that analogous 2-acyl-4-imino-4*H*-1,3-oxazines are stable for the both skeleton types, *i.e.* for benzo and thieno systems[13], as electroneutral molecules. We have assumed that the chalcogenazinium skeleton is formed in acidic media as a product of thermodynamically controlled reaction.

Cyclization described for acylthiourea analogues of **5a**–**5f** with pyrimidine skeleton may be initiated by the action of a base, *e.g.* ammonia, sodium or potassium carbonate, alcoholate or hydroxide in water or water–alcohol solution[5,7,8,11]. In dependence on basicity of the reaction mixture and reaction temperature, the cyclization proceeds together with deacylation (under harder conditions) or without elimination of the acyl group (under mild conditions and with benzo skeleton). In the second case, Dimroth rearrangement follows the cyclization and 4-acylaminoquinazoline derivatives are formed.

The action of anhydrous methanolic solution of potassium hydroxide on **5a**–**5f** led to the formation of potassium salts **9a**–**9f** (Scheme 3). We have assumed that deprotonation of the nitrogen atom of acylamino group predominated. The formed anion is thermodynamically more stable than that formed by deprotonation of the amino group in the heterocyclic skeleton as a consequence of delocalization of negative charge in the $[C(Se)NC(O)]^-$ fragment.

Using one equivalent of potassium hydroxide in methanolic solution at room temperature, potassium salts of the thiophene series **9b**, **9c**, **9e** and **9f** were isolated. Unlike with the sulfur analogues, their separation was successful due to their limited solubility.

On the other hand, potassium salts **9a** and **9d** of the benzo series were well soluble in the reaction mixture and were not obtained in crystalline state. Attempts of their precipitation by an addition of small amounts of solvents such as benzene, dichloromethane or their mixtures with petro-

leum ether were unsuccessful. The salts **9a** and **9d** were separated as tar products.

In FTIR spectra of **9b**, **9c**, **9e** and **9f** corresponding vibrational bands of NHCO and NHCSe groups were not found. On the other hand, two very intensive bands were observed at 1 460 and 1 340 cm^{-1} and were assigned as the stretching vibration bands of the deprotonated acylselenoureido $[C(Se)NC(O)]^-$ group.

Standing at room temperature or a short reflux of methanolic solution containing the *in situ* prepared salts **9a**, **9d**, caused their transformation to 4-aminoquinazoline-2-selenol (**11a**). On the other hand, suspensions of **9b**, **9c**, **9e** and **9f** in methanol gave under reflux deacylated non-cyclic products, which were identified as isoselenoureas **10b** and **10c** (Scheme 3).

We have assumed that acylselenoureas of the benzo series **5a** and **5d** react analogously. However, due to their higher reactivity, they cyclize spontaneously to the quinazoline skeleton. Similar reaction was observed during the addition of ammonia to 2-isoselenocyanatobenzonitrile[25] or its sulfur analogue[26]. The adducts formed *in situ* already cyclized at temperature lower than 0 °C. The corresponding selenoureas or thioureas were not isolated. The rate of deacylation is slower and thus the step probably controls the complex reaction.

In FTIR spectra of **10b** and **10c**, intensive C=N vibrations were observed, but vibrational bands of the selenoamide group were not found. The chemical shift of the $^{13}C(Se)$ signal with a lower value than 170 ppm together with the value of the ^{13}C-^{77}Se coupling showed that this carbon is bonded to selenium by a single bond like in acylisoselenoureas[1]. The compounds **10b** and **10c** exist mainly in the tautomeric 3-isoselenoureido form as confirmed by ^1H NMR spectra as only one type of protons is observed. The existence of tautomeric 1-isoselenoures form was not confirmed.

The lower reactivity of the thieno *versus* benzo derivatives in cyclization under basic conditions was found also in the case of analogous thioureas[22].

If the reaction mixture containing salts **9a**–**9f** suspended or dissolved in methanol was refluxed in the presence of an excess of potassium hydroxide, cyclization and deacylation proceeded under formation of corresponding potassium pyrimidine-2-selenolate. After acidification of the reaction mixture, fused 4-aminopyrimidine-2-selenoles **11a** and **11b** and 4-amino-5,6-dimethyl-1,2-dihydrothieno[2,3-*d*]pyrimidine-2-selon **12c**, respectively, crystallized as free bases.

The structures of fused pyrimidines **11a**–**11c** and **12a**–**12c** synthesized by cyclization of **5a**–**5f** or **10a**–**10c** in basic medium were confirmed by elemental analysis, FTIR, ^1H and ^{13}C NMR spectroscopy. FTIR and ^{13}C NMR

spectra of the products showed that compounds **11a** and **11b** are stable under the experimental conditions as the pyrimidine-2-selenol whereas compound **12c** as a selenoxo compound. NMR spectra were measured in deuterotrifluoroacetic acid solution due to their low solubility in other solvents. The ^{13}C Se signal of compounds **11a** and **11b** was overlapped by a signal of carbonyl carbon using trifluoroacetic acid (δ 163.24–164.31 ppm) and its value could not be determined.

It is well known that thioureas similar to isoselenoureas **10b** and **10c** by heating cyclize to pyrimidines[27]. In the case of **10b** and **10c**, the cyclization need not be initiated thermally. Their cycloaddition proceeded only by the action of base at higher temperature. We have assumed the existence of deprotonated Se–H group. A higher acidity of this group in comparison with the terminal amino group is given by higher thermodynamically stability of the formed selenoate anion. After redistribution of electron density, the pyrimidine skeleton is formed as a product of thermodynamical controlled reaction under the used conditions.

The found results indicate a different course of base-initiated cyclization of acylselenoureas and their sulfur analogues. The later can be used preparatively[8], kinetic methods[28] confirmed that deacylation proceeded after the pyrimidine skeleton formation.

EXPERIMENTAL

Chemicals and reagents were purchased from Fluka Chemie Co. and used without purification. 2-Aminothiophene-3-carbonitriles **4b** and **4c** were prepared by the modified Gewald method[29] in dimethylformamide in yields 80 and 92% (ref.[29] gives 42 and 39%), respectively. Melting points were measured on a Boetius Rapido PHMK 79/2106 (Wägetechnik) instrument and are not corrected. CHN elemental analyses were made on an instrument 1102 (Erba), selenium was determined on a spectrometer ICP AES 7500 (Unicam). TLC was carried out on Silufol UV 254 plates (Kavalier, Votice) using UV detection or visualization with iodine vapors and elution with chloroform, diethyl ether or acetonitrile. The FTIR spectra were taken on a spectrometer Genesis (Unicam) in potassium bromide pellets. NMR spectra were measured in deuteriochloroform ($CDCl_3$), hexadeuteriodimethyl sulfoxide ($(CD_3)_2SO$) or in deuteriotrifluoroacetic acid (CF_3COOD) on a Bruker Avance DRX-500 spectrometer. The ^{13}C and ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to the solvent signals of $CDCl_3$ and of residual $CHCl_3$ at 77.00 (^{13}C) and 7.27 ppm (^{1}H), respectively. The ^{77}Se NMR chemical shifts were referenced to H_2SeO_3 (1 282 ppm) or $SeOCl_2$ (1 479 ppm), the ^{15}N NMR chemical shifts were referenced to liquid ammonia (0 ppm) used as external standards. Spectral width: 9 000 Hz for ^{1}H, 27 500 Hz for ^{13}C and 38 000 Hz for ^{77}Se. HETCOR and COLOC spectra were measured using Bruker standard sequences. In the ^{1}H-^{15}N HMBC[30–33], ^{1}H-^{15}N GSQMBC[33, 34], ^{1}H-^{77}Se HMBC[34] and ^{1}H-^{77}Se GSQMBC[34] experiments pulsed-field-gradients were used for coherence selection. For experiment optimization, see refs[1,30–34]. The measured ^{13}C and ^{1}H NMR spectra were correlated with those

obtained by on-line simulation (Advanced Chemistry Development, Inc., Toronto, Canada). The X-ray structural data of compound **5b** (Table V) were collected with a KUMA KM-4 kappa four-circle diffractometer. The structure was solved by direct methods using SHELXS86 (ref.[35]) and refined on F^2 for all reflections using SHELXL93 (ref.[36]). Crystals suitable for X-ray determination were obtained by crystallization from water-saturated chloroform in the form of yellow triclinic plates. Geometry optimization of structures **5b** and **5e** were performed at *ab initio* level of quantum chemical calculation, RHF/DZVP and

TABLE V
Crystal data and structure refinement for compound **5b**

Empirical formula	$C_{34}H_{32}N_6O_3S_2Se_2$
Molecular weight	794.70
Temperature, K	288 (2)
Wavelength, Å	0.71073
Crystal system, space group	triclinic, *P1*
Unit cell dimensions	
a, Å; α, °	10.370(2); 102.084(13)
b, Å; β, °	12.444(2); 104.444(13)
c, Å; γ, °	13.794(2); 94.319(14)
Volume, Å^3	1 670.2(5)
Z; density calculated, mg m^{-3}	2; 1.580
Absorption coefficient, mm^{-1}	2.384
F(000)	804
Crystal size, mm	0.80 × 0.40 × 0.20
θ range for data collection, °	1.57–25.05
Range of *h*, *k*, *l*	–12→0, –14→14, –15→16
Reflections collected	6 204
Independent reflections	5 923 [*R*(int) = 0.0270]
Refinement method	full-matrix least-squares on F^2
Data; restraints; parameters	5 921; 0; 462
Goodness-of-fit on F^2	0.977
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.0528, *wR2* = 0.1411
R indices (all data)	*R1* = 0.1213, *wR2* = 0.1846
Maximum and minimum heights in final Δρ map	1.061; –0.984

DFT/VWN/DZVP, respectively. Mass spectra were taken on a spectrometer Mat 445 (Varian) in the CI mode using a CH_4/N_2O mixture as ionizing gas. All syntheses mentioned below, except cyclization reaction in acid media, were performed under inert gases (nitrogen or argon) in order to avoid selenium oxidation with atmospheric oxygen.

General Procedures for Preparation of Compounds **5a**–**5f**

Method A. Potassium selenocyanate (7.63 g, 53 mmol) was dissolved in acetone (50 ml, dried 24 h with anhydrous calcium chloride and distilled) under stirring at room temperature. Benzoyl chloride (7.45 g, 53 mmol) or 2,2-dimethylpropanoyl chloride (6.39 g, 53 mmol) dissolved in acetone (20 ml) was added dropwise. The reaction mixture was stirred for 10 min, the precipitated potassium chloride was filtered off and washed with acetone (10 ml). An acetone solution of the corresponding 2-aminonitrile (50 mmol) was added to the benzoyl- or 2,2-dimethylpropanoylisoselenocyanate solution and the mixture was stirred at room temperature. After 15–30 min (TLC) the reaction mixture was evaporated to dryness and the crude product dissolved in chloroform at a temperature about 4 °C. The formed suspension was filtered with charcoal, the filtrate separated from colloid selenium and concentrated to 1/5 original volume and mixed with an equivalent of petroleum ether. The precipitated crystals were filtered off, washed with petroleum ether and cold methanol. The product was dried *in vacuo*.

Method B. Oligomeric benzoylisoselenocyanate (4.60 g, 25 mmol) was added to the suspension of amine **4a**–**4c** (20 mmol) was suspended in toluene (30 ml) and the reaction mixture was refluxed 45–60 min (TLC control). After the reaction, the hot mixture was filtered through silica gel, the filtrate was cooled and the crude separated products (**5a**–**5f**) were purified as mentioned above.

2-(3-Benzoylselenoureido)benzonitrile (**5a**). Yield: (*A*) 13.7 g (83%), (*B*) 5.0 g (75%); m.p. 153–155 °C (methanol). For $C_{15}H_{11}N_3OSe$ (328.2) calculated: 54.89% C, 3.38% H, 12.80% N, 24.92% Se; found: 54.92% C, 3.32% H, 12.74% N, 24.36% Se. MS, *m/z* (%): 328 (16, M^+), 329 (8, $(M + 1)^+$), 248 (98, $(M - SeH)^+$), 226 (35, $(PhCONHCSeNH)^+$), 223 (10, $(M - PhCO)^+$), 222 (8, $(M - HSeCN)^+$), 106 (10, $(HSeCN)^+$), 105 (100, $(PhCO)^+$). FTIR: 3 325, 3 195 (NH), 2 210 (C≡N), 1 650, 1 540 (NHCO, amide I, II), 1 515, 932 (NHCSe, selenoamide I, III). ^{1}H NMR ($CDCl_3$): 7.45–8.19 m, 9 H (H-arom.); 9.66 s, 1 H (NHCO); 13.28 s, 1 H (NHCSe). ^{13}C NMR ($CDCl_3$): 109.63 (C-1), 115.84 (C≡N), 127.20 (C-3), 127.81 (C-2′ and C-6′, C_6H_5), 127.91 (C-5), 129.28 (C-3′ and C-5′, C_6H_5), 130.88 (C-1′, C_6H_5), 133.22 (C-6), 133.44 (C-4), 134.16 (C-4′, C_6H_5), 141.31 (C-2), 167.08 (C=O), 182.55 J(C,Se) = 225. ^{77}Se NMR ($CDCl_3$): 481.

2-(3-Benzoylselenoureido)-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carbonitrile (**5b**). Yield: (*A*) 18.1 g (93%), (*B*) 6.05 g (78%); m.p. 201–204 °C (methanol). For $C_{17}H_{15}N_3OSSe$ (388.4) calculated: 52.08% C, 3.89% H, 10.82% N, 20.54% Se; found: 51.97% C, 3.80% H, 10.70% N, 20.49% Se. MS, *m/z* (%): 388 (19, M^+), 389 (7, $(M + 1)^+$), 308 (95, $(M - SeH)^+$), 283 (10, $(M - PhCO)^+$), 282 (10, $(M - HSeCN)^+$), 226 (38, $(PhCONHCSeNH)^+$), 106 (8, $(HSeCN)^+$), 105 (100, $(PhCO)^+$). FTIR: 3 380, 3 260 (NH), 2 200 (C≡N), 1 650, 1 560 (NHCO, amide I, II), 1 512, 975 (NHCSe, selenoamide I, III). ^{1}H NMR ($CDCl_3$): 1.85–1.86 m, 4 H (5-CH_2 and 6-CH_2); 2.65 t, 2 H, J(4-CH_2) = 5.0; 2.67 t, 2 H, J(7-CH_2) = 6.0; 7.55–7.92 m, 5 H (C_6H_5); 9.53 s, 1 H (NHCO); 14.69 s, 1 H (NHCSe). ^{13}C NMR ($CDCl_3$): 22.06 (C-5), 23.01 (C-6), 23.92 (C-4), 24.25 (C-7), 100.02 (C-3), 113.71 (C≡N), 127.83 (C-2′ and C-6′, C_6H_5), 129.31 (C-3′ and C-5′, C_6H_5), 129.63 (C-4, thiophene), 130.60 (C-5, thiophene), 132.24 (C-1′, C_6H_5), 134.24 (C-4′,

C_6H_5), 147.29 (C-2, thiophene), 167.15 (C=O), 175.72 *J*(C,Se) = 223. ^{15}N NMR ($CDCl_3$): 151.7 (NCSe), 155.2 (C≡N), 162.3 (NCO). ^{77}Se NMR ($CDCl_3$): 482. For X-ray analysis, see Results and Discussion.

2-(3-Benzoylselenoureido)-4,5-dimethylthiophene-3-carbonitrile (**5c**). Yield: (*A*) 15.2 g (84%), (*B*) 5.2 g (72%); m.p. 112–115 °C (methanol). For $C_{15}H_{13}N_3OSSe$ (326.3) calculated: 49.73% C, 3.62% H, 11.60% N, 22.02% Se; found: 49.43% C, 3.55% H, 11.40% N, 21.95% Se. MS, *m/z* (%): 362 (15, M^+), 282 (100, $(M - SeH)^+$), 257 (5, $(M - PhCO)^+$), 256 (11, $(M - HSeCN)^+$), 226 (40, $(PhCONHCSeNH)^+$), 106 (10, $(HSeCN)^+$), 105 (95 $(PhCO)^+$). FTIR: 3 273, 3 180 (NH), 2 217 (C≡N), 1 670, 1 555 (NHCO, amide I, II), 1 519, 970 (NHCSe, selenoamide I, III). ^{1}H NMR ($CDCl_3$): 2.24 s, 3 H (CH_3, C-4 thiophene); 2.29 s, 3 H (CH_3, C-5 thiophene); 7.56–7.95 m, 5 H (C_6H_5); 9.47 s, 1 H (NHCO); 14.68 s, 1 H (NHCSe). ^{13}C NMR ($CDCl_3$): 12.40 (CH_3, C-4 thiophene), 12.78 (CH_3, C-5 thiophene), 101.95 (C-3, thiophene), 114.08 (C≡N), 126.50 (C-4, thiophene), 127.81 (C-2′and C-6′, C_6H_5), 129.34 (C-3′and C-5′, C_6H_5), 130.03 (C-5, thiophene), 130.61 (C-1′, C_6H_5), 134.26 (C-4′, C_6H_5), 146.28 (C-2, thiophene), 167.11 (C=O), 175.63 *J*(C,Se) = 222. ^{77}Se NMR ($CDCl_3$): 481.

2-[3-(2,2-Dimethylpropanoyl)selenoureido]benzonitrile (**5d**). Yield: (*A*) 12.6 g (82%); m.p. 146–148 °C (methanol). For $C_{13}H_{15}N_3OSe$ (308.2) calculated: 50.66% C, 4.90% H, 13.36% N, 25.86% Se; found: 50.50% C, 4.58% H, 11.40% N, 25.94% Se. MS, *m/z* (%): 308 (18, M^+), 309 (8, $(M + 1)^+$), 228 (100, $(M - SeH)^+$), 235 (6, $(M - (CH_3)_3CCO)^+$), 202 (11, $(M - HSeCN)^+$), 194 (41, $((CH_3)_3CCONHCSeNH)^+$), 106 (5, $(HSeCN)^+$), 73 (95, $((CH_3)_3CCO)^+$). FTIR: 3 412, 3 187 (NH), 2 229 (C≡N), 1 678, 1 550 (NHCO, amide I, II), 1 503, 963 (NHCSe, selenoamide I, III). ^{1}H NMR ($CDCl_3$): 1.34 s, 9 H ($C(CH_3)_3$); 7.43–8.14 m, 4 H (C_6H_4); 9.05 s, 1 H (NHCO); 13.49 s, 1 H (NHCSe). ^{13}C NMR ($CDCl_3$): 28.86 (CH_3, $C(CH_3)_3$), 40.05 ($C(CH_3)_3$), 109.51 (C-1), 115.73 (C≡N), 127.12 (C-3), 127.84 (C-5), 133.17 (C-6), 133.27 (C-4), 141.25 (C-2), 179.63 (C=O), 182.68 *J*(C,Se) = 225. ^{77}Se NMR ($CDCl_3$): 411.

2-[3-(2,2-Dimethylpropanoyl)selenoureido]-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carbonitrile (**5e**). Yield: (*A*) 16.4 g (89%); m.p. 178–180 °C. For $C_{15}H_{19}N_3OSSe$ (368.3) calculated: 48.91% C, 5.20% H, 11.41% N, 21.66% Se; found: 48.78% C, 5.04% H, 11.32% N, 21.60% Se. MS, *m/z* (%): 368 (16, M^+), 288 (100, $(M - SeH)^+$), 295 (10, $(M - (CH_3)_3CCO)^+$), 262 (8, $(M - HSeCN)^+$), 194 (38, $((CH_3)_3CCONHCSeNH)^+$), 106 (6, $(HSeCN)^+$), 73 (98, $((CH_3)_3CCO)^+$). FTIR: 3 285, 3 190 (NH), 2 200 (C≡N), 1 675, 1 555 (NHCO, amide I, II), 1 510, 960 (NHCSe, selenoamide I, III). ^{1}H NMR ($CDCl_3$): 1.33 s, 9 H ($C(CH_3)_3$); 1.82–1.83 m, 4 H (5-CH_2 and 6-CH_2); 2.65 t, 2 H, *J*(4-CH_2) = 5.0; 2.66 t, 2 H, *J*(7-CH_2) = 6.0; 8.92 s, 1 H (NHCO), 14.53 s, 1 H (NHCSe). ^{13}C NMR ($CDCl_3$): 22.00 (C-6), 22.95 (C-5), 23.82 (C-4), 24.16 (C-7), 26.86 (CH_3, $C(CH_3)_3$), 40.04 ($C(CH_3)_3$), 99.93 (C-3), 113.58 (C≡N), 129.58 (C-4, thiophene), 132.17 (C-5, thiophene), 147.24 (C-2, thiophene), 179.75 (C=O), 179.75 *J*(C,Se) = 223. ^{15}N NMR ($CDCl_3$): 151.7 (NCSe), 155.2 (C≡N), 161.8 (NCO). ^{77}Se NMR ($CDCl_3$): 465.

2-[3-(2,2-Dimethylpropanoyl)selenoureido]-4,5-dimethylthiophene-3-carbonitrile (**5f**). Yield: (*A*) 13.1 g (77%); m.p. 163–165 °C (methanol). For $C_{13}H_{17}N_3OSSe$ (342.3) calculated: 46.51% C, 5.01% H, 12.28% N, 23.30% Se; found: 46.37 % C, 4.98% H, 12.03% N, 23.37% Se. MS *m/z* (%): 342 (16, M^+), 262 (100, $(M - SeH)^+$), 269 (8, $M - (CH_3)_3CCO)^+$), 236 (7, $(M - HSeCN)^+$), 194 (32, $((CH_3)_3CCONHCSeNH)^+$), 106 (8, $(HSeCN)^+$), 73 (98, $((CH_3)_3CCO)^+$). FTIR: 3 344, 3 220 (NH), 2 211 (C≡N), 1 640, 1 567 (NHCO, amide I, II), 1 503, 931 (NHCSe, selenoamide I, III). ^{1}H NMR ($CDCl_3$): 1.34 s, 9 H ($C(CH_3)_3$); 2.22 s, 3 H (CH_3, C-4 thiophene); 2.27 s, 3 H (CH_3, C-5 thiophene); 8.93 s, 1 H (NHCO); 14.53 s, 1 H (NHCSe). ^{13}C NMR ($CDCl_3$): 12.24 (CH_3, C-4 thiophene), 12.62 (CH_3, C-5 thiophene), 26.76 (CH_3, $C(CH_3)_3$), 39.93 ($C(CH_3)_3$),

101.55 (C-3, thiophene), 113.84 (C≡N), 126.25 (C-4, thiophene), 129.76 (C-5, thiophene), 146.18 (C-2, thiophene), 179.65 (C=O), 175.70 *J*(C,Se) = 222. ^{77}Se NMR ($CDCl_3$): 466.

General Procedure for Preparation of Compounds **6a**–**6f**

Nitrile **5a**–**5f** (10 mmol) was dissolved at the room temperature in a 50 ml of anhydrous methanol solution of hydrogen chloride saturated at 20–25 °C. The reaction mixture was stirred at room temperature until crystal formation appeared (60–120 min). Then the reaction mixture was left to crystallize in an icebox. The product was separated by suction, washed with methanol and diethyl ether and dried *in vacuo* at room temperature.

2-Benzoylamino-4-imino-4H-benzo[3,1]selenazinium chloride (**6a**). Yield: 3.2 g (86%); m.p. 251–252 °C (ether). For $C_{15}H_{12}ClN_3OSe$ (364.6) calculated: 49.40% C, 3.32% H, 11.52% N, 21.64% Se; found: 48.95% C, 3.17% H, 11.38% N, 21.58% Se. FTIR: 3 375 (NH), 1 660 (amide I), 1 642 (N–C$^+$(Se)–N), 1 624 (C=N), 1 567 (amide II), 1 277 (amide III). ^{1}H NMR (CF_3COOD): 7.53 d, 1 H, *J*(C8-H) = 7.61; 7.76–7.99 m, 5 H (C_6H_5CO); 8.17–8.18 m, 1 H (C6-H); 8.23-8.25 m, 1 H (C7-H); 8.50 d, 1 H, *J*(C5-H) = 7.63. ^{13}C NMR (CF_3COOD): 121.23 (CH), 126.81(CH), 127.21 (CH), 128.13 (CH), 132.20 (CH), 133.22 (CH), 136.20 (C), 138.92 (C), 139.41 (C), 139.78 (C), 153.80 (C=N), 160.90 *J*(N–C$^+$–Se) = 161, 175.76 (C=O).

2-Benzoylamino-4-imino-5,6,7,8-tetrahydro-4H-benzo[1]thieno[2,3-d][1,3]selenazinium chloride (**6b**). Yield: 4.0 g (95%); m.p. 196–198 °C (ether). For $C_{17}H_{16}ClN_3OSSe$ (424.8) calculated: 48.07% C, 3.80% H, 9.89% N, 18.58% Se; found: 47.94% C, 3.69% H, 9.45% N, 18.53% Se. MS, *m/z* (%): 388 (35, (M – HCl)$^+$), 308 (40, (338 – SeH)$^+$), 226 (19, (PhCONHCSeNH)$^+$), 105 (100 (PhCO)$^+$). FTIR: 3 200 (NH), 1 657 (amide I), 1 650 (N–C$^+$(Se)–N), 1 638 (C=N), 1 570 (amide II), 1 260 (amide III.). ^{1}H NMR (CF_3COOD): 2.03–2.09 m, 4 H (5-CH_2 and 6-CH_2); 2.93–2.95 m, 2 H (4-CH_2); 2.99–3.08 m, 2 H (7-CH_2); 7.63–7.67 m, 2 H (C_6H_5CO); 7.79–7.82 m, 1 H (C_6H_5CO); 7.97–8.08 m, 2 H (C_6H_5CO). ^{13}C NMR (CF_3COOD): 23.17 (CH_2), 23.54 (CH_2), 26.47 (CH_2), 28.71 (CH_2), 128.23 (CH), 130.46 (C), 131.04 (C), 131.25 (C), 132.25 (CH), 137.50 (CH), 140.88 (C), 156.76 (C=N), 156.93 *J*(N–C$^+$–Se) = 171, 172.84 (C=O).

2-Benzoylamino-4-imino-5,6-dimethyl-4H-thieno[2,3-d][1,3]selenazinium chloride (**6c**). Yield: 2.8 g (71%); m.p. 202–205 °C (ether). For $C_{15}H_{14}ClN_3OSSe$ (398.8) calculated: 45.18% C, 3.54% H, 10.54% N, 19.79% Se; found: 44.89% C, 3.48% H, 10.42% N, 19.74% Se. FTIR: 3 200 (NH), 1 655 (amide I), 1 650 (N–C$^+$(Se)–N), 1 630 (C=N), 1 575 (amide II), 1 272 (amide III). ^{1}H NMR (CF_3COOD): 2.72 s, 3 H (CH_3); 2.82 s, 3 H (CH_3); 7.75–8.25 m, 5 H (C_6H_5CO). ^{13}C NMR (CF_3COOD): 13.51 (CH_3), 15.51 (CH_3), 126.12 (C), 126.78 (C), 129.01 (CH), 130.05 (C), 131.32 (C), 133.12 (CH), 135.65 (CH), 138.40 (C), 153.08 (C=N), 164.22 *J*(N–C$^+$–Se) = 168, 177.51 (C=O).

4-Imino-2-2,2-dimethylpropanoylamino-4H-benzo[3,1]selenazinium chloride (**6d**). Yield: 3.0 g (87%); m.p. 186–189 °C (ether). For $C_{13}H_{16}ClN_3OSe$ (344.7) calculated: 45.30% C, 4.68% H, 12.19% N, 22.89% Se; found: 45.23% C, 4.52% H, 11.97% N, 22.82% Se. FTIR: 3 315 (NH), 1 694 (amide I), 1 652 (N–C$^+$(Se)–N), 1 630 (C=N), 1 575 (amide II), 1 260 (amide III). ^{1}H NMR (CF_3COOD): 1.18 s, 9 H ((CH_3)$_3$C); 8.25 d, 1 H, *J*(C8-H) = 7.61; 8.31–8.34 m, 1 H (C7-H); 8.67–8.71 m, 1 H (C6-H); 8.91 d, 1 H, *J*(C5-H) = 7.63.). ^{13}C NMR (CF_3COOD): 27.62 (CH_3, (CH_3)$_3$C), 41.09 (C), 127.58 (C), 132.80 (C), 141.85 (C), 142.09 (C), 157.00 (C=N), 175.83 *J*(N–C$^+$–Se) = 154, 186.19 (C=O).

4-Imino-2-(2,2-dimethylpropanoyl)amino-5,6,7,8-tetrahydro-4H-benzo[1]thieno[2,3-d][1,3]selenazinium chloride (**6e**). Yield: 3.8 g (95%); m.p. 106–107 °C (ether). For $C_{15}H_{20}ClN_3OSSe$ (404.8) calculated: 44.51% C, 4.98% H, 10.38% N, 19.49% Se; found: 44.42% C, 4.86% H,

10.27% N, 19.44% Se. FTIR: 3 233 (NH), 1 675 (amide I), 1 653 (N–C^+(Se)–N), 1 635 (C=N), 1 572 (amide II), 1 266 (amide III). ^{1}H NMR (CF_3COOD): 1.48 s, 9 H (($CH_3)_3C$); 1.95–2.12 m, 4 H (5-CH_2 and 6-CH_2); 2.91–2.98 m, 2 H (4-CH_2); 3.02-3.10 m, 2 H (7-CH_2). ^{13}C NMR (CF_3COOD): 23.47 (CH_2), 24.03 (CH_2), 26.41 (CH_2), 27.69 (CH_3, $(CH_3)_3C$), 28.63 (CH_2), 42.01 (C), 130.30 (C), 130.43 (C), 133.73 (C), 140.63 (C), 156.78 (C=N), 177.72 *J*(N–C^+–Se) = 151, 185.83 (C=O).

4-Imino-5,6-dimethyl-2-(2,2-dimethylpropanoyl)amino-4H-thieno[2,3-d][1,3]selenazinium chloride (**6f**). Yield: 2.9 g (77%); m.p. 137–138 °C (ether). For $C_{13}H_{18}ClN_3OSSe$ (378.8) calculated: 41.22% C, 4.79% H, 11.09% N, 20.83% Se; found: 41.04% C, 4.73% H, 10.89% N, 20.79% Se. FTIR: 3 315 (NH), 1 667 (amide I), 1 650 (N–C^+(Se)–N), 1 642 (C=N), 1 547 (amide II), 1 273 (amide III). ^{1}H NMR (CF_3COOD): 1.49 s, 9 H (($CH_3)_3C$); 2.57 s, 3 H (CH_3); 2.66 s, 3 H (CH_3). ^{13}C NMR (CF_3COOD): 13.51 (CH_3), 15.51 (CH_3), 27.45 (CH_3, $(CH_3)_3C$), 42.11 (C), 126.05 (C), 126.55 (C), 130.05 (C), 138.40 (C), 155.05 (C=N), 176.83 *J*(N–C^+–Se) = 159, 186.12 (C=O).

General Procedure for Preparation of Compounds **7a**–**7f**

Compound **5a**–**5f** (10 mmol) was dissolved in 96% sulfuric acid (25 ml) at 5–10 °C and the mixture was left to cyclize at room temperature. After 1 h, the reaction mixture was poured onto crashed ice (100 g). The insoluble portion was filtered off, washed successively with methanol and diethyl ether, and then dried *in vacuo* at room temperature.

2-Benzoylamino-4-imino-4H-benzo[3,1]selenazinium hydrogensulfate (**7a**). Yield: 3.7 g (87%); m.p. 269–270 °C (ether). For $C_{15}H_{13}N_3O_5SSe$ (426.3) calculated: 42.26% C, 3.07% H, 9.89% N, 18.51% Se; found: 41.98% C, 2.95% H, 9.66% N, 18.43% Se. FTIR: 3 200 (NH), 1 650 (amide I, N–C^+(Se)–N), 1 638 (C=N), 1 570 (amide II), 1 260 (amide III), 1 142, 1 085, 874 (HSO_4^-).

2-Benzoylamino-4-imino-5,6,7,8-tetrahydro-4H-benzo[1]thieno[2,3-d][1,3]selenazinium hydrogensulfate (**7b**). Yield: 4.2 g (86%); m.p. 265–269 °C (ether). For $C_{17}H_{17}N_3O_5S_2Se$ (486.4) calculated: 41.98% C, 3.52% H, 8.64% N, 16.22% Se; found: 41.56% C, 3.48% H, 8.53% N, 15.99% Se. FTIR: 3 200 (NH), 1 650 (amide I, N–C^+(Se)–N), 1 638 (C=N), 1 570 (amide II), 1 260 (amide III), 1 137, 1 073, 872 (HSO_4^-).

2-Benzoylamino-4-imino-5,6-dimethyl-4H-thieno[2,3-d][1,3]selenazinium hydrogensulfate (**7c**). Yield: 3.9 (85%); m.p. 254–256 °C (ether). For $C_{15}H_{15}N_3OSSe$ (460.4) calculated: 39.13% C, 3.28% H, 9.13% N, 17.14% Se; found: 38.12% C, 3.42% H, 8.94% N, 16.87% Se. FTIR: 3 200 (NH), 1 650 (amide I, N–C^+(Se)–N), 1 630 (C=N), 1 575 (amide II), 1 272 (amide III), 1 140, 1 079, 870 (HSO_4^-).

4-Imino-2-(2,2-dimethylpropanoyl)amino-4H-benzo[3,1]selenazinium hydrogensulfate (**7d**). Yield: 3.8 g (94%); m.p. 186–189 °C (ether). For $C_{13}H_{17}N_3O_5SSe$ (406.4) calculated: 38.43% C, 4.22% H, 10.34% N, 19.42% Se; found: 38.12% C, 3.99% H, 9.98% N, 19.36% Se. MS, *m/z* (%): 308 (30, $(M - H_2SO_4)^+$), 228 (43, $(308 - SeH)^+$), 194 (15, $((CH_3)_3CCONHCSeNH)^+$), 73 (100, $((CH_3)_3CCO)^+$). FTIR: 3 315 (NH), 1 694 (amide I, N–C^+(Se)–N), 1 630 (C=N), 1 575 (amide II), 1 260 (amide III), 1 150, 1 081, 872 (HSO_4^-).

4-Imino-2-(2,2-dimethylpropanoyl)amino-5,6,7,8-tetrahydro-4H-benzo[b]thieno[2,3-d][1,3]selenazinium hydrogensulfate (**7e**). Yield: 4.0 g (86%); m.p. 162–165 °C (ether). For $C_{15}H_{21}N_3O_5S_2Se$ (466.4) calculated: 38.63% C, 4.54% H, 9.01% N, 16.92% Se; found: 38.46% C, 4.37% H, 9.06% N, 16.74% Se. FTIR: 3 233 (NH), 1 653 (amide I, N–C^+(Se)–N), 1 635 (C=N), 1 572 (amide II), 1 266 (amide III), 1 135, 1 075, 864 (HSO_4^-).

4-Imino-5,6-dimethyl-2-(2,2-dimethylpropanoyl)amino-4H-thieno[2,3-d][1,3]selenazinium hydrogensulfate (**7f**). Yield: 3.9 g (84%); m.p. 186–188 °C (ether). For $C_{13}H_{19}N_3O_5S_2Se$ (440.6) calculated: 35.46% C, 4.35% H, 9.54% N, 17.92% Se; found: 35.19% C, 4.06% H, 9.33% N, 17.76% Se. FTIR: 3 315 (NH), 1 667 (amide I, N–C^+(Se)–N), 1 642 (C=N), 1 547 (amide II), 1 273 (amide III), 1 139, 1 075, 869 (HSO_4^-).

General Procedure for Preparation of Compounds **8a**–**8f**

A solution of compound **7a**–**7f** (5 mmol) in sulfuric acid was added at 5–10 °C into a 40% aqueous solution of tetrafluoroboric acid (25 ml). The products were separated as mentioned above.

2-Benzoylamino-4-imino-4H-3,1-benzo[3,1]selenazinium tetrafluoroborate (**8a**). Yield: 1.4 g (67%); m.p. 254–257 °C (ether). For $C_{15}H_{12}BF_4N_3OSe$ (416.0) calculated: 43.30% C, 2.91% H, 10.10% N, 18.97% Se; found: 42.98% C, 2.83% H, 10.02% N, 18.81% Se. FTIR: 3 200 (NH), 1 650 (amide I, N–C^+(Se)–N), 1 638 (C=N), 1 570 (amide II), 1 260 (amide III), 1 164 (BF_4^-).

2-Benzoylamino-4-imino-5,6,7,8-tetrahydro-4H-benzo[1]thieno[2,3-d][1,3]selenazinium tetrafluoroborate (**8b**). Yield: 1.5g (70%); m.p. 235–240 °C (ether). For $C_{17}H_{16}BF_4N_3OSSe$ (426.2) calculated: 42.88% C, 3.39% H, 8.82% N, 16.57% Se; found: 42.50% C, 3.24% H, 8.64% N, 16.38% Se. FTIR: 3 200 (NH), 1 650 (amide I, N–C^+(Se)–N), 1 638 (C=N), 1 570 (amide II), 1 260 (amide III), 1 167 (BF_4^-).

2-Benzoylamino-4-imino-5,6-dimethyl-4H-thieno[2,3-d][1,3]selenazinium tetrafluoroborate (**8c**). Yield: 1.5 (72%); m.p. 194–195 °C (ether). For $C_{15}H_{14}BF_4N_3OSSe$ (450.1) calculated: 40.03% C, 3.13% H, 9.34% N, 17.53% Se; found: 39.63% C, 3.06% H, 9.26% N, 17.43% Se. FTIR: 3 200 (NH), 1 650 (amide I, N–C^+(Se)–N), 1 630 (C=N), 1 575 (amide II), 1 272 (amide III), 1 175 (BF_4^-).

4-Imino-2-(2,2-dimethylpropanoyl)amino-4H-benzo[3,1]selenazinium tetrafluoroborate (**8d**). Yield: 1.3 g (66%); m.p. 192–195 °C (ether). For $C_{13}H_{16}BF_4N_3OSe$ (396.1) calculated: 39.42% C, 4.07% H, 10.61% N, 19.92% Se; found: 39.06% C, 3.98% H, 10.49% N, 19.63% Se. FTIR: 3 315 (NH), 1 694 (amide I, N–C^+(Se)–N), 1 630 (C=N), 1 575 (amide II), 1 260 (amide III), 1 162 (BF_4^-).

4-Imino-2-(2,2-dimethylpropanoyl)amino-5,6,7,8-tetrahydro-4H-benzo[1]thieno[2,3-d][1,3]selenazinium tetrafluoroborate (**8e**). Yield: 1.6 g (77%); m.p. 117–120 °C (ether). For $C_{15}H_{20}BF_4N_3OSSe$ (456.2) calculated: 39.50% C, 4.42% H, 9.21% N, 17.30% Se; found: 39.12% C, 4.35% H, 9.16% N, 17.19% Se. FTIR: 3 233 (NH), 1 653 (amide I, N–C^+(Se)–N), 1 635 (C=N), 1 572 (amide II), 1 266 (amide III), 1 172 (BF_4^-).

4-Imino-5,6-dimethyl-2-(2,2-dimethylpropanoyl)amino-4H-thieno[2,3-d][1,3]selenazinium tetrafluoroborate (**8f**). Yield: 1.4 g (65%); m.p. 141–143 °C (ether). For $C_{13}H_{18}BF_4N_3OSSe$ (430.1) calculated: 36.30% C, 4.22% H, 9.77% N, 18.35% Se; found: 36.06% C, 3.89% H, 9.60% N, 18.21% Se. FTIR: 3 315 (NH), 1 667 (amide I, N–C^+(Se)–N), 1 642 (C=N), 1 547 (amide II), 1 273 (amide III),), 1 160 (BF_4^-).

Retrocyclization Reactions of **6a**–**6f**, **7a**–**7f** and **8a**–**8f** to **5a**–**5f**. General Procedure

Compound **6a**–**6f**, **7a**–**7f** and **8a**–**8f** (5 mmol) was suspended in water (50 ml) and the pH value of the mixture was adjusted to 7–8 with a 5% aqueous solution of potassium carbonate. After about 5 min, the product was extracted to chloroform (2 × 20 ml) and the extract was dried with anhydrous sodium sulfate. The solution was concentrated to 1/3 of its original volume and mixed with an equal volume of petroleum ether. The precipitated crystals

were filtered, washed with petroleum ether and cold methanol (5–10 °C). The pure product was dried *in vacuo*. The yields were in the range of 90–95%. The obtained nitriles **5a**–**5f** were identical with standards by TLC, m.p., FTIR and ^{1}H NMR spectra.

General Procedure for Preparation of Compounds **9b**, **9c**, **9e** and **9f**

Compound **5b**, **5c**, **5e** or **5f** (5 mmol) was dissolved at room temperature under stirring in a solution of potassium hydroxide (340 mg, 6 mmol) in methanol (50 ml). After 30 min, the corresponding product (**9b**, **9c**, **9e** or **9f**) was separated by suction, washed with methanol, diethyl ether and dried *in vacuo* at room temperature.

2-(3-Benzoylselenoureido)-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carbonitrile potassium salt (**9b**). Yield: 1.8 g (85%); m.p. 201–202 °C (decomp.). For $C_{17}H_{14}N_3OSSeK$ (462.4) calculated: 47.88% C, 3.31% H, 9.85% N, 18.50% Se; found: 47.43% C, 3.15% H, 9.63% N, 18.42% Se. FTIR: 3 204, 3 165 (NH), 2 215 (C≡N), 1 460 (NCO), 1 350 (NCSe). ^{1}H NMR ($(CD_3)_2SO$): 1.62–1.75 m, 4 H (5-CH_2 and 6-CH_2); 2.14–2.15 m, 2 H (4-CH_2); 2.73–2.75 m, 2 H (7-CH_2); 4.30 s, 1 H (NH); 7.25–8.40 m, 5 H (C_6H_5). ^{13}C NMR ($(CD_3)_2SO$): 22.46 (C-5), 23.35 (C-6), 24.00 (C-4), 24.25 (C-7), 92.82 (C-3), 114.63 (C-4, thiophene), 116.71 (C≡N), 127.23 (C-2′ and C-6′, C_6H_5), 129.04 (C-3′ and C-5′, C_6H_5), 130.72 (C-5, thiophene), 130.24 (C-1′, C_6H_5), 133.42 (C-4′, C_6H_5), 157.09 (C-2, thiophene), 160.33 (C=O), 171.95 *J*(C=Se) = 180.

2-(3-Benzoylselenoureido)-4,5-dimethylthiophene-3-carbonitrile potassium salt (**9c**). Yield: 1.65 g (84%); m.p. 292–293 °C (decomp.). For $C_{15}H_{12}N_3OSSeK$ (400.4) calculated: 45.00% C, 3.02% H, 10.49% N, 19.71% Se; found: 44.87% C, 2.97% H, 10.24% N, 19.46% Se. FTIR: 3 348, 3 318 (NH), 2 200 (C≡N), 1 458 (NCO), 1 339 (NCSe). ^{1}H NMR ($(CD_3)_2SO$): 2.13 s, 3 H (CH_3, C-4 thiophene); 2.21 s, 3 H (CH_3, C-5 thiophene); 7.39–7.88 m, 5 H (C_6H_5); 8.27 s, 1 H (NH).

2-[3-(2,2-Dimethylpropanoyl)selenoureido]-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carbonitrile potassium salt (**9e**). Yield: 1.6 g (79%); m.p. 185–188 °C (decomp.). For $C_{15}H_{18}N_3OSSeK$ (406.5) calculated: 44.33% C, 4.46% H, 10.43% N, 19.42% Se; found: 44.19% C, 4.15% H, 10.37% N, 19.36% Se. FTIR: 3 200, 3 182 (NH), 2 225 (C≡N), 1 468 (NCO), 1 338 (NCSe). ^{1}H NMR ($(CD_3)_2SO$): 1.16 s, 9 H (CH_3, $C(CH_3)_3$); 1.17–1.24 m, 4 H (5-CH_2 and 6-CH_2); 2.14–2.15 m, 2 H (4-CH_2); 2.62–2.69 m, 2 H (7-CH_2); 8.84 s, 1 H (NH).

2-[3-(2,2-Dimethylpropanoyl)selenoureido)-4,5-dimethylthiophene-3-carbonitrile potassium salt (**9f**). Yield: 1.4 g (74%); m.p. 188–200 °C (decomp.). For $C_{13}H_{16}N_3OSSeK$ (380.4) calculated: 41.05% C, 4.24% H, 11.05% N, 20.74% Se; found: 39.98% C, 4.12% H, 11.06% N, 20.38% Se. FTIR: 3 221, 3 060 (NH), 2 204 (C≡N), 1 459 (NCO), 1 350 (NCSe). ^{1}H NMR ($(CD_3)_2SO$): 1.21 s, 9 H (CH_3, $(CH_3)_3C$); 2.03 s, 3 H (CH_3, C-4 thiophene); 2.16 s, (CH_3, C-5 thiophene); 7.95 s, 1 H (NH).

General Procedure for Preparation of Compounds **10b** and **10c**

Potassium salt **9b**, **9c**, **9e** or **9f** (2.5 mmol) was suspended in anhydrous methanol (20–30 ml) and refluxed for 10 min. The corresponding product (**10b**, **10c**), which crystallized from the reaction mixture after staying overnight in a freezing box, was separated by suction and recrystallized from ethanol (charcoal).

2-(3-Isoselenoureido)-4,5,6,7-tetrahydrobenzo[1]thiophene-3-carbonitrile (**10b**). Yield: 0.5 g (70%) (from **9b**), 0.55 g (77%) (from **9e**); m.p. 202–205 °C (ethanol). For $C_{10}H_{11}N_3SSe$ (285.0) calculated: 42.26% C, 3.90% H, 14.78% N, 27.79% Se; found: 41.95% C, 3.81% H,

14.68% N, 27.47% Se. FTIR: 3 248, 3 188 (NH), 2 200 (C≡N), 1 650 (C=N). ^{1}H NMR ($CDCl_3$): 1.56 bs, 3 H (SeH and NH_2); 1.81–1.84 m, 4 H (5-CH_2 and 6-CH_2); 2.73–2.94 m, 4 H (4-CH_2 and 7-CH_2). ^{13}C NMR ($CDCl_3$): 22.96 (C-6), 24.80 (C-5), 26.21 (C-7), 27.11 (C-4), 89.38 (C-3), 122.59 (C≡N), 131.15 (C-5 thiophene), 131.28 (C-4 thiophene), 163.07 (C-2), 168.74 *J*(N=C–Se) = 154.

2-(3-Isoselenoureido)-4,5-dimethylthiophene-3-carbonitrile (**10c**). Yield: 0.6 g (84%) (from **9c**), 0.6 g (84%) (from **9f**); m.p. 182–186 °C (ethanol). For $C_8H_9N_3SSe$ (259.0) calculated: 37.07% C, 3.50% H, 16.22% N, 30.56% Se; found: 36.89% C, 3.46% H, 15.97% N, 30.29% Se. FTIR: 3 249, 3 197 (NH), 2 207 (C≡N), 1 652 (C=N). ^{1}H NMR ($CDCl_3$): 1.58 bs, 3 H (SeH and NH_2); 2.33 s, 3 H (CH_3, C-4 thiophene); 2.46 s, 3 H (CH_3, C-5 thiophene). ^{13}C NMR ($CDCl_3$): 12.63 (CH_3, C-4 thiophene), 14.24 (CH_3, C-5 thiophene), 94.88 (C-3, thiophene), 120.56 (C≡N), 129.24 (C-5, thiophene), 131.71 (C-4, thiophene), 165.65 (C-2, thiophene), 169.45 *J*(N=C–Se) = 147.

General Procedures for Preparation of Compounds **11a**–**11c** and **12a**–**12c**

Method A. Acylselenourea **5a**–**5f** (5 mmol) was suspended in a 5% methanolic solution of potassium hydroxide (50 ml) and refluxed until a clear solution was formed (5–10 min). The solution was filtered with charcoal, until filtrate was cooled to 5–10 °C and neutralized with glacial acetic acid. The precipitated product (**11a**–**11c** and **12a**–**12c**) was filtered off, washed with methanol and dried *in vacuo*.

Method B. Isoselenourea **10b** or **10c** (2 mmol) was suspended in 5% methanol solution of potassium hydroxide (20 ml) and refluxed (5–10 min). Then the solution was treated as described in method *A*.

Method C. 2-(3-Acylselenoureido)benzonitrile **5a** or **5d** (5 mmol) was dissolved in 30 ml methanol solution of potassium hydroxide (340 mg, 6 mmol) at room temperature. The solution was stirred at room temperature for 20 min or under reflux for 5 min (TLC). After cooling, the precipitated 4-aminoquinazoline-2-selenol (**11a**) was filtered off, washed with methanol and dried *in vacuo*.

4-Aminoquinazoline-2-selenol (**11a**). Yield: (*A*, from **5a**) 0.9 g (80%), (*A*, from **5d**) 0.9 g (80%), (*C*, from **5a**) 0.85 g (76%), (*C*, from **7**) 0.8 g (72%); m.p. 25–259 °C (methanol). For $C_8H_7N_3Se$ (224.1) calculated: 42.87% C, 3.15% H, 18.75% N, 35.21% Se; found: 42.46% C, 3.09% H, 18.51% N, 34.98% Se. FTIR: 3 300, 3 127 (NH_2), 1 643 (C=N). ^{1}H NMR (CF_3COOD): 7.84–8.37 m, 4 H (C_6H_4). ^{13}C NMR (CF_3COOD): 112.74 (C-5, pyrimidine), 120.65 (C-5), 126.50 (C-8), 132.30 (C-6), 140.48 (C-7), 141.42 (C-6, pyrimidine), 159.50 (C-4).

4-Amino-5,6,7,8-tetrahydrobenzo[1]thieno[2,3-d]pyrimidine-2-selenol (**11b**): Yield: (*A*, from **5b**) 1.30 g (91%), (*A*, from **5e**) 1.20 g (84%), (*B*, from **10b**) 0.40 g (70%); m.p. 292–295 °C (methanol). For $C_{10}H_{11}N_3SSe$ (285.0) calculated: 42.26% C, 3.90% H, 14.783% N, 27.76% Se; found: 41.88% C, 3.76% H, 14.56% N, 27.54% Se. FTIR: 3 381, 3 212 (NH), 1 645 (C=N). ^{1}H NMR (CF_3COOD): 1.82–2.20 m, 4 H (6-CH_2 and 7-CH_2); 2.85–3.09 m, 4 H (5-CH_2 and 8-CH_2). ^{13}C NMR (CF_3COOD): 23.61 (C-7), 23.75 (C-6), 24.05 (C-8), 31.77 (C-5), 130.23 (C-10, cyclohexane), 132.47 (C-9, cyclohexane), 137.09 (C-5, pyrimidine), 139.01 (C-6, pyrimidine), 153.49 (C-4).

4-Amino-5,6-dimethylthieno[2,3-d]pyrimidine-2-(1H)-selone (**12c**): Yield: (*A*, from **5c**) 1.10 g (85%), (*A*, from **5f**) 1.10 g (85%), (*B*, from **10c**) 0.35 g (67%); m.p. 199–202 °C (methanol). For $C_8H_9N_3SSe$ (258.9) calculated: 37.07% C, 3.50% H, 16.22% N, 30.56% Se; found: 36.79% C,

3.49% H, 16.16% N, 30.42% Se. FTIR: 3 440, 3 293 (NH), 1 622 (C=N), 1 527, 954 (NHCSe, selenoamide III, I). ^{1}H NMR (CF_3COOD): 2.82 s, 3 H (CH_3); 2.83 s, 3 H (CH_3). ^{13}C NMR (CF_3COOD): 11.12 (CH_3, C-5), 11.80 (CH_3, C-6), 126.51 (C-5), 132.91 (C-6), 152.48 (C-5, pyrimidine), 155.16 (C-4), 169.71 (C-6, pyrimidine), 181.29 *J*(C=Se) = 220.

This work was supported by the Grant Agency of the Czech Republic (grants No. 203/93/0715, No. 203/96/0111 and No. 203/96/1513). We would like to thank Biosym/Molecular Simulations of San Diego for providing us with the academic license for the InsightII and Turbomole software. We thank the Academic Supercomputer centre in Brno for access to the computer facilities. Our thanks are also due to Dr J. Jambor of Department of Analytical Chemistry of the Faculty for determination of selenium by Inductively Coupled Plasma – Atomic Emission Spectrometry, to the Analytical department of Lachema Co., Brno, Czech Republic for elemental analysis, MS Laboratory of Université Catholique Louvain, Louvain-la-Neuve, Belgium for measuring mass spectra and Advanced Chemistry Development, Inc., Toronto, Canada for the free on-line simulation of ^{1}H and ^{13}C NMR spectra.

REFERENCES

1. Pazdera P., Šibor J., Marek R., Kutý M., Marek J.: *Molecules* **1997**, *2*, 135.
2. Dobosh A. A., Kripak S. M., Smolanka I. V.: *Khim. Geterotsikl. Soedin.* **1974**, 486.
3. Yul L. M., Yangibaev V. Yu., Alekseeva L. N.: *Khim. Geterotsikl. Soedin.* **1987**, 1095.
4. Chan, Chao-Han, Shish, Fang-Jy: *Heterocycles* **1987**, *26*, 3193.
5. Sauter F., Deinhammer W.: *Monatsh. Chem.* **1973**, *104*, 159.
6. Leistner S., Gütschow M., Wagner G., Grupe R., Böhme B.: *Pharmazie* **1988**, *43*, 466.
7. Leistner S., Gütschow M., Wagner G.: *Arch. Pharm. (Weinheim)* **1989**, *322*, 227.
8. Leistner S., Gütschow M.: *Z. Chem.* **1990**, *30*, 23.
9. Gütschow M., Leistner S.: *Z. Chem.* **1990**, *30*, 440.
10. Leistner S., Gütschow M., Stach J.: *Arch. Pharm. (Weinheim)* **1990**, *323*, 857.
11. Pazdera P., Potůček V., Nováček E., Kalviňš I., Trapencieris P., Pugovics O.: *Chem. Pap.* **1991**, *45*, 527.
12. Pazdera P., Preissová I.: *Chem. Pap.* **1992**, *46*, 396.
13. Šibor J.: *M.S. Thesis*. Masaryk University, Brno 1995.
14. Šibor J., Pazdera P., Pichler J.: *Chem. Pap.*, submitted.
15. Douglas I. B.: *J. Am. Chem. Soc.* **1937**, *59*, 740.
16. Bulka E., Ahlers K.-D.: *Z. Chem.* **1963**, *3*, 387.
17. Bendito D. P., Casillas J., Pino F.: *Inform. Quim. Anal. (Madrid)* **1966**, *20*, 69; *Chem. Abstr.* **1966**, *65*, 19304.
18. a) Bulka E. in: *Chemistry of Cyanates and Their Thio Derivatives* (S. Patai, Ed.), Part 2, p. 887. Wiley, New York 1977; b) Bulka E., Ehlers D., Storm E.: *Z. Chem.* **1970**, *10*, 380.
19. Horák M., Papoušek D.: *Infračervená spektra a struktura molekul*, p. 640. Academia, Praha 1996.
20. Ref.[19], p. 705.
21. Marek R., Králík L., Humpa O., Šibor J., Pazdera P., Sklenář V.: Unpublished results.
22. Pazdera P.: *Habilitation Thesis*. Masaryk University, Brno 1992.
23. Pazdera P., Potůček V.: *Chem. Pap.* **1991**, *45*, 677.
24. Pazdera P., Preissová I.: Unpublished results.
25. Pazdera P., Havránek M.: Unpublished results.

26. Pazdera P., Ondráček D., Nováček E.: *Chem. Pap.* **1989**, *43*, 771.
27. Pazdera P., Řezka M., Nováček E.: *Chem. Pap.* **1990**, *44*, 63.
28. a) Kaválek J., Macháček V., Said El Bahaie, Štěrba V.: *Collect. Czech. Chem. Commun.* **1981**, *42*, 246; b) Kaválek J., Macháček V., Sedlák M., Štěrba V.: *Collect. Czech. Chem. Commun.* **1993**, *58*, 1122.
29. a) Gewald K., Schinke E., Böttcher H.: *Chem. Ber.* **1966**, *99*, 94; b) Gewald K., Schinke E.: *Chem. Ber.* **1966**, *99*, 2712.
30. Bax A., Summers M. F.: *J. Am. Chem. Soc.* **1986**, *108*, 2093.
31. Willker W., Leibfritz D., Kerssebaum R., Bermel W.: *Magn. Reson. Chem.* **1993**, *31*, 287.
32. Martin G. E., Crouch R. C., Sharaf M. H. M., Schiff P. L., Jr.: *J. Nat. Prod.* **1996**, *59*, 2.
33. Marek R.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 1747.
34. Marek R., Králík L., Sklenář V.: *Tetrahedron Let.* **1997**, *38*, 665.
35. Sheldrick G. M.: *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **1990**, *46*, 467.
36. Sheldrick G. M.: *SHELXL93: Program for Structure Refinement*. University of Göttingen, Göttingen 1993.