Synthesis of 4-(Phenylamino)quinazoline-2(1*H*)-selones and Diselenides from Isoselenocyanates: *Dimroth* Rearrangement of an Intermediate

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The reaction of anthranilonitriles **8** with phenyl isoselenocyanates (**1a**) in dry pyridine under reflux gave 4-(phenylamino)quinazoline-2(1*H*)-selones **9** (*Scheme 2*). They are easily oxidized and converted to diselenides of type **11**. The analogous reaction of **8a** with phenyl isothiocyanate (**1b**) yielded the quinazoline-2(1*H*)-thione **10** (*Scheme 2*). A reaction mechanism *via* a *Dimroth* rearrangement of the primarily formed intermediate is presented in *Scheme 3*. The molecular structures of **10** and **11a** have been established by X-ray crystallography. Unexpectedly, no selone or diselenide was obtained in the case of the reaction with 3-aminobenzo[*b*]furan-2-carbonitrile (**14**). The only product isolated was the selenide **16** (*Scheme 4*), the structure of which has been established by X-ray crystallography.

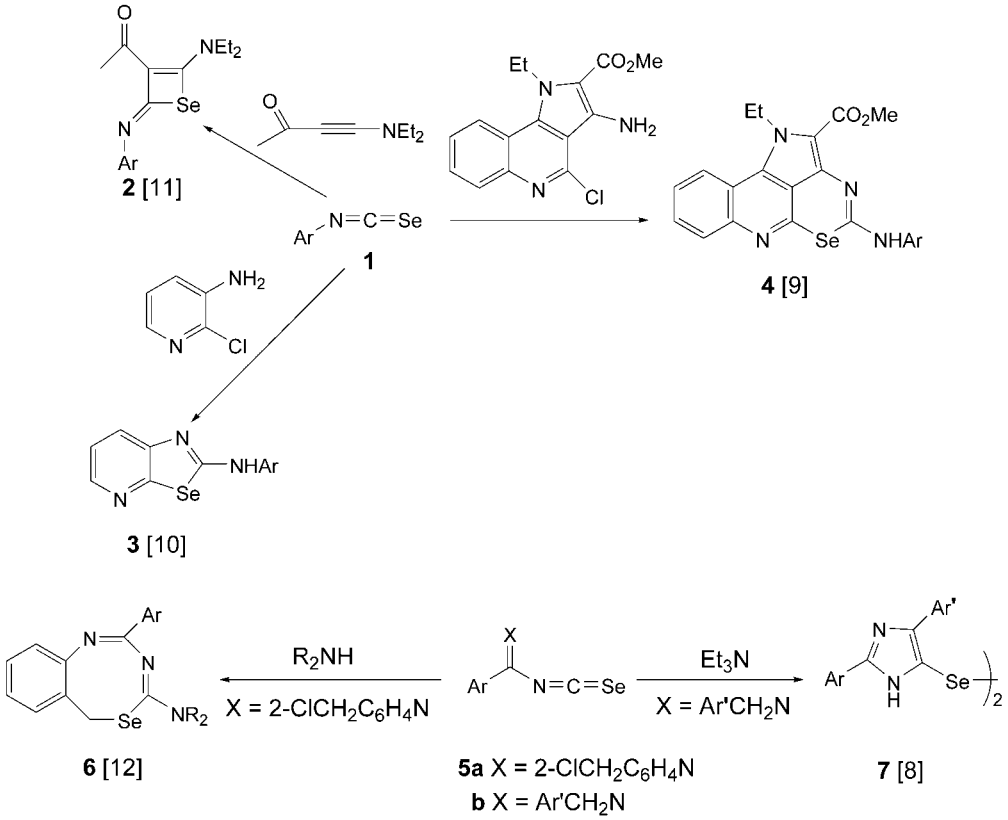
1. Introduction. – In recent years, the interest in the chemistry of Se-containing compounds has increased remarkably due to their chemical properties [1–4] and biological activities [5–7] (see also refs. cit. in [8–12]). Selenium, for a long time recognized as dietary antioxidant [13], is now known to be an essential component of the active sites of several enzymes, including glutathione peroxidase [14] and thioredoxin reductase [15], which catalyze reactions essential for the protection of cellular components against oxidative and free radical damage. This is a good basis for the development of novel pharmaceutical agents that contain selenium or that target specific aspects of selenium metabolism. Among them are orally active antihypertensive, anticancer, antiviral, and immunosupressive organoselenium compounds, as well as those that reduce oxidative tissue damage and endema [16]. *Hatfield* [17] discussed a large body of evidence that indicates that selenium is a cancer-chemopreventive agent. Further evidence points to its role in preventing heart disease, and other cardiovascular and muscle disorders, and in delaying the progression of AIDS in HIV-infected patients.

For these reasons, the design and synthesis of organoselenium compounds, especially Se-containing heterocycles, are of current interest [18–26]. It has been shown that isoselenocyanates are versatile Se reagents for the preparation of selenaheterocycles, *e.g.*, benzo[*b*]selenophenes [27], 1,2,3-selenadiazoles [28][29], selenapentalenes [30], 1,3-diselenol-2-imines [31], and 1,3-selenazoles [32]. In some other cases, heteropolycyclic selones were the products [33][34]. Recently, we have shown that aryl isoselenocyanates **1** are convenient precursors for the introduction of Se into four- (**2**) [11], five- (**3**) [10], and six-membered selenaheterocycles (**4**) [9]

[1]) Part of the Ph.D. Thesis of *P. K. A.*, Universität Zürich, 2004.

(*Scheme 1*). Furthermore, *N*-arylbenzimidoyl isoselenocyanates **5a** on treatment with primary or secondary amines gave 6*H*-[5,1,3]benzoselenadiazocines **6** [12], whereas *N*-(4-nitrobenzyl)benzimidoyl isoselenocyanates **5b** underwent a base-catalyzed cyclization and an oxidative dimerization to yield di(imidazol-5-yl) diselenides **7** [8] (*Scheme 1*).

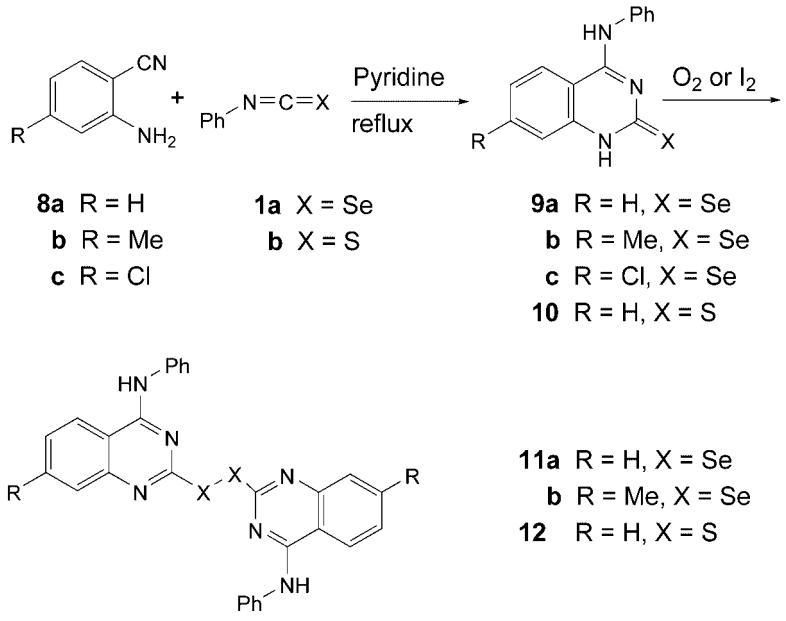
Scheme 1



In the present paper, we report on the reaction of phenyl isoselenocyanate (**1a**) with anthranilonitriles (2-aminobenzonitriles). The analogous reaction of anthranilonitrile with phenyl isothiocyanate to give 1,2-dihydro-4-(phenylamino)quinazoline-2-thione has already been reported by *Taylor* and *Ravindranathan* [35] and by *Pazdera et al.* [36].

2. Results and Discussion. – To a solution of the corresponding 2-aminobenzonitrile **8** in anhydrous pyridine, *ca.* 1 equiv. of freshly prepared phenyl isoselenocyanate (**1a**) was added, and the mixture was heated to reflux for 2.5 h. After evaporation of the solvent, the residue was triturated with MeOH, and a yellowish crystalline product was obtained in the cases of **9a**–**9c** (*Scheme 2*). The analogous reaction of **8a** with phenyl isothiocyanate (**1b**) led to the corresponding thione **10**, which has been described previously [35]. The structures of **9** and **10**, *i.e.*, 4-(phenylamino)quinazoline-2(1*H*)-

Scheme 2



selones and 4-(phenylamino)quinazoline-2(1*H*)-thione, respectively, were confirmed by their NMR, MS, and IR data, and elemental analyses. In the case of **10**, the structure was established by X-ray crystallography (*Fig. 1*).

The asymmetric unit contains one molecule of **10** and one MeOH molecule. The entire molecule of **10** is almost completely planar, with the largest deviation from the least-squares plane being 0.062(2) Å for C(14). The N(1)H group in the six-membered ring forms an intermolecular H-bond with the S-atom of an adjacent molecule **10**. This interaction links pairs of **10** into centrosymmetric dimers, which have a graph set motif [38] of $R_2^2(8)$. The exocyclic N(4)H group forms an intermolecular H-bond with the O-atom of MeOH, which, in turn, forms a H-bond with the S-atom of a different molecule of **10**. These interactions link the moieties into centrosymmetric tetramers composed of two molecules **10** and two MeOH molecules. The tetramers have a graph set motif of $R_4^4(16)$. The combination of all H-bonding interactions results in extended chains, which run parallel to the [101] direction, where the links in the chain are alternately the dimeric and the tetrameric units.

All attempts to obtain single crystals of the selone **9a** failed. During recrystallization from MeCN, oxidative dimerization to give diselenide **11a** occurred in almost quantitative yield (*Scheme 2*). It is worth mentioning that the formation of **11b** from **9b** took place more slowly; the conversion was realized in good yield by bubbling O_2 through a solution of **9b** in pyridine at room temperature. The S analogue **10** was even more stable, and no disulfide was obtained after treatment with O_2. Finally, the oxidation was successful when a solution of **10** in pyridine was treated with I_2 at room temperature.

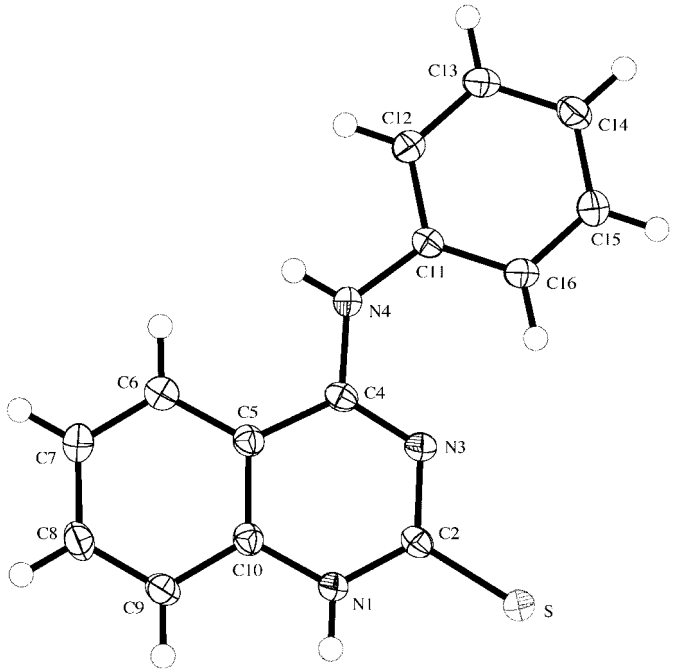


Fig. 1. *ORTEP Plot* [37] *of the molecular structure of* **10** (arbitrary numbering of the atoms; 50% probability ellipsoids)

The structure of **11a** was again established by X-ray crystallography (*Fig. 2*). Single crystals of **11a** were obtained by crystallization from MeCN. In one of several attempts, a single crystal of a minor product (< 5%) was also isolated. The structure of this product was established as triselenide **13** (*Fig. 2*).

The asymmetric unit of **11a** contains one diselenide molecule and two MeOH molecules. The bond lengths within the pyrimidine ring, plus the exocyclic C–N bond indicate significant delocalization of the π-electrons in these regions of the molecule. The coordination about N(4) and N(20) is trigonal planar rather than tetrahedral, and the torsion angles N(3)–C(4)–N(4)–C(11) and N(19)–C(20)–N(20)–C(27) are 5.9(5) and 5.5(5)°, respectively. However, the Ph rings at N(4) and N(20) are twisted significantly out of the plane of the heterocycle (the torsion angles C(4)–N(4)–C(11)–C(12) and C(20)–N(20)–C(27)–C(32) are −32.1(5) and 38.4(5)°, resp.). The two heterocyclic moieties of **11a** are almost orthogonal to each other, with the mean planes of the fused-ring systems intersecting at an angle of 81.88(9)°. This is the result of the torsion angle of the diselenide bond C(2)–Se(1)–Se(2)–C(18) being −91.4(1)°. Turns of *ca.* 90° about chalcogenic bonds are quite common for both oligosulfides [39] and oligoselenides. A search of the January 2004 issue of the *Cambridge Structural Database* [40] revealed reliable structures ($R < 0.075$) for 80 neutral acyclic organic oligoselenides from which 92 independent structural fragments of the type X–Se–Se–X (X = any element, including a further Se-atom) were obtained. The absolute value of the X–Se–Se–X

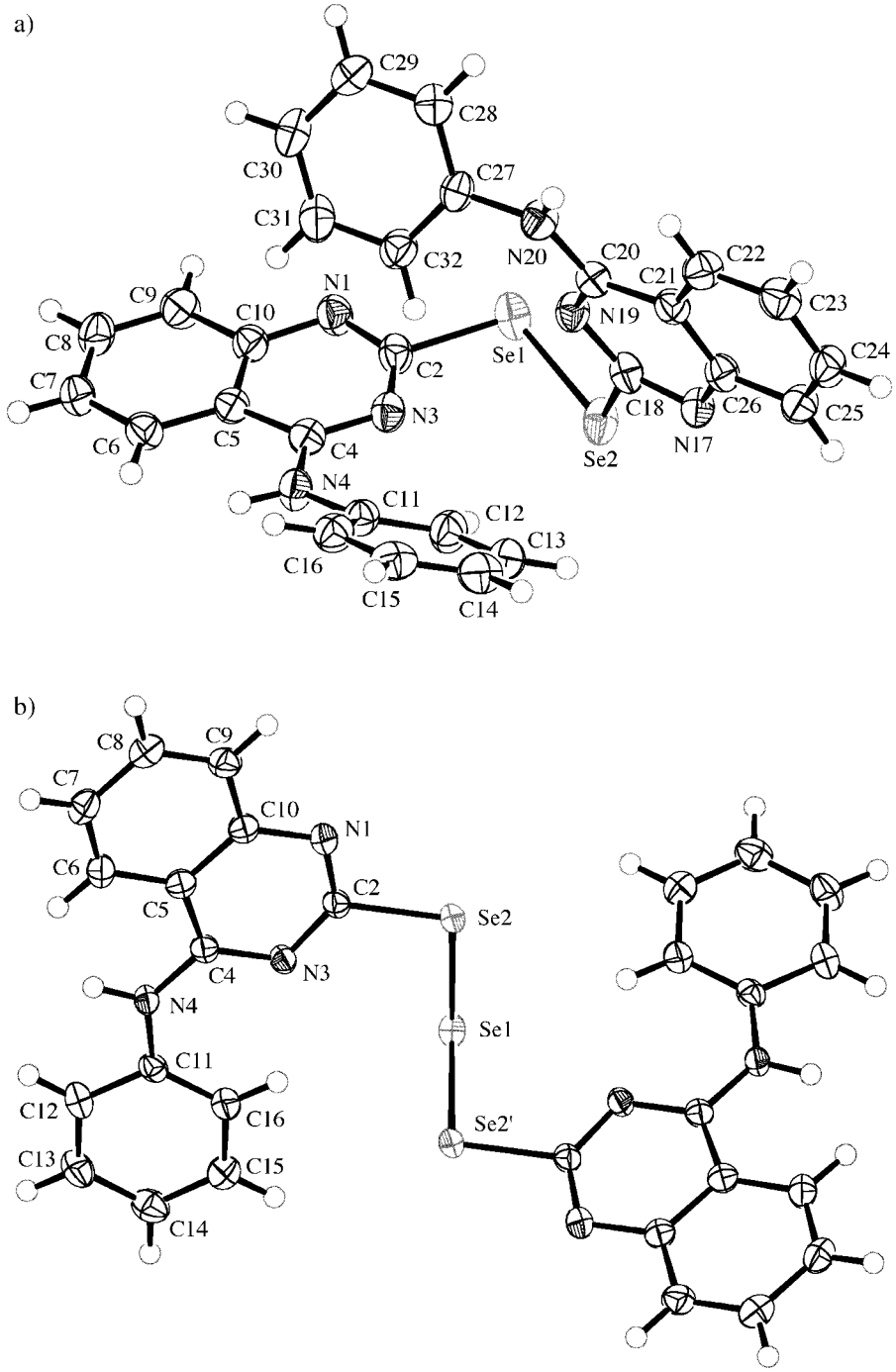
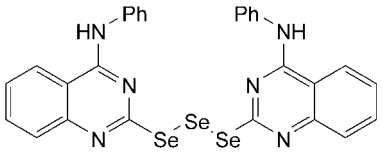


Fig. 2. *ORTEP Plots* [37] *of the molecular structure of* a) **11a** and b) **13** (arbitrary numbering of the atoms; 50% probability ellipsoids)

torsion angle is clearly clustered around 90° with 70 of the 92 fragments lying in the range 72–105°. Another eleven conformations have torsion angles close to 180. Each of the two NH groups, N(4)H and N(20)H, of **11a** forms an intermolecular H-bond with a different symmetry-independent neighboring MeOH molecule. These MeOH molecules, in turn, form intermolecular H-bonds with N(17) and N(1), respectively, of the pyrimidine rings of other diselenide molecules. Considering the route through one of the symmetry-independent MeOH molecules, the H-bonding interactions link **11a** and the MeOH molecule alternately into extended chains, which run parallel to the *z*-axis and have a graph set motif of C(11). The route through the other MeOH molecule forms identical chains, but these chains run parallel to the *y*-axis. The combination of all H-bonding interactions links the molecules into an infinite two-dimensional network that lies parallel to the *yz*-plane.



13

The molecules of **13** possess crystallographic C_2 symmetry with the twofold axis passing through the central Se-atom, and the asymmetric unit includes one H_2O molecule. Although **13** is achiral, the compound has crystallized in a non-centrosymmetric polar space group, and the absolute structure has been determined confidently by refinement of the absolute structure parameter. Similar to the disulfide **11a**, the two heterocyclic moieties of **13** are almost orthogonal to each other, with the mean planes of the fused-ring systems intersecting at an angle of 74.34(7)°. As discussed above for **11a**, the X–Se–Se–X torsion angles (equal by symmetry) are again close to 90° (C(2)–Se(2)–Se(1)–Se(2′) −84.98(7)°). Each NH group of **13** forms an intermolecular H-bond with the O-atom of an adjacent H_2O molecule, so that one molecule of **13** interacts with two H_2O molecules. In turn, the H_2O molecule acts as a donor for two intermolecular H-bonds, one involving the ring-bonded Se-atom of a second molecule of **13**, while the other involves one of the ring N-atoms from a third molecule of **13**. The N–H ··· O–H ··· N interactions, combined with the twofold symmetry of **13**, link the molecules into infinite two-dimensional networks. The N–H ··· O–H ··· Se interactions cross-link these two dimensional networks to form a three-dimensional H-bonded framework overall.

In analogy to the formation of 4-(phenylamino)quinazoline-2(1*H*)-thione (**10**) [35][36], a reaction mechanism for the formation of the Se-analogues **9** is proposed in *Scheme 3*. Addition of the NH_2 group of **8** to **1a** leads to the selenourea derivative **A**, which undergoes a ring closure to give **B** (or its tautomer). The S analogues of **A** and **B** have been described as products of the reaction of **8a** and **1b** at 50° (without solvent) and in boiling benzene, respectively [35][36][2]). An isomerization *via* ring opening to **C**

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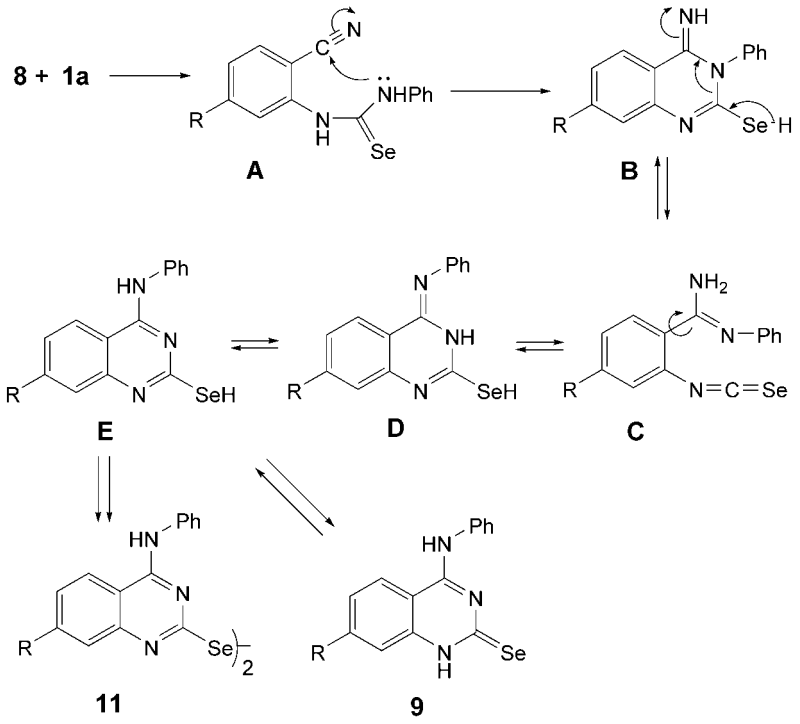
[2]) In these two references, divergent observations are reported. Some results described in [35], *e.g.*, the formation of the S-analogue of **A**, could not be reproduced [36].

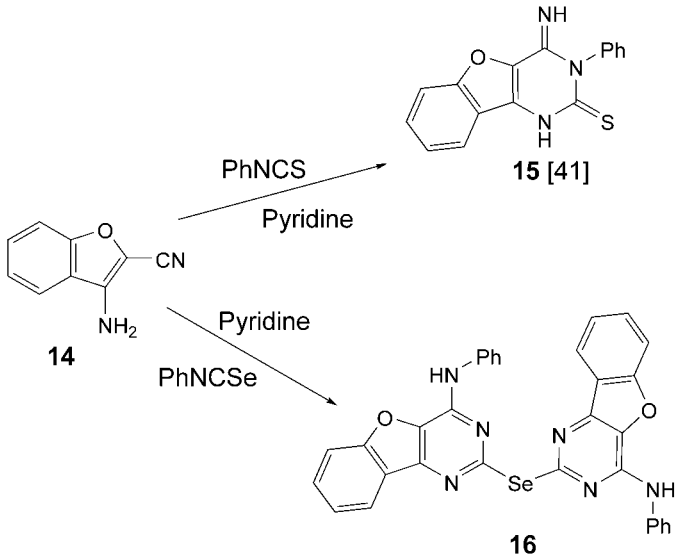
Scheme 3



and a new ring closure leads to **D**, which tautomerizes to give **9**, similar to the *Dimroth* rearrangement [41]. Whereas the analogous isomerization has been reported by *Taylor* and *Ravindranathan* [35], it did not occur under similar conditions according to *Pazdera et al.* [36]. The latter authors obtained the imino derivative of type **B** as a stable compound. On the other hand, the reaction of **8a** and **1b** in refluxing pyridine, carried out by us, led exclusively to **10**, the structure of which has unequivocally been established by X-ray crystallography.

Recently, *Sangapure* and *Mulagi* reported that the reaction of phenyl isothiocyanate (**1b**) with 3-aminobenzo[*b*]furane-2-carbonitrile (**14**) [42] gave the benzofuro[3,2-*d*]-pyrimidine derivative **15** [43] (*Scheme 4*). When we carried out the reaction of **14** with phenyl isoselenocyanate (**1a**) in refluxing pyridine, we obtained only one product, which showed an $[M+1]^+$ peak at *m*/*z* 601 (ESI-MS). The NMR spectra indicated a symmetrical structure with two benzofuro[3,2-*d*]pyrimidine rings. Finally, an X-ray crystal-structure determination established structure **16** (*Fig. 3*). In both halves of the molecule, the pyrimidine ring bears a PhNH group. Therefore, a *Dimroth* rearrangement of the initially formed product with an imino and an *N*-phenyl group had occurred, similar to the reaction sequence depicted in *Scheme 3*. The most remarkable feature of the structure is the presence of only one Se atom. Although we are not able to offer a convincing reaction mechanism for the formation of **16**, Se–C Bond formation according to **F** or **G** could be proposed. Another possibility is the

Scheme 4



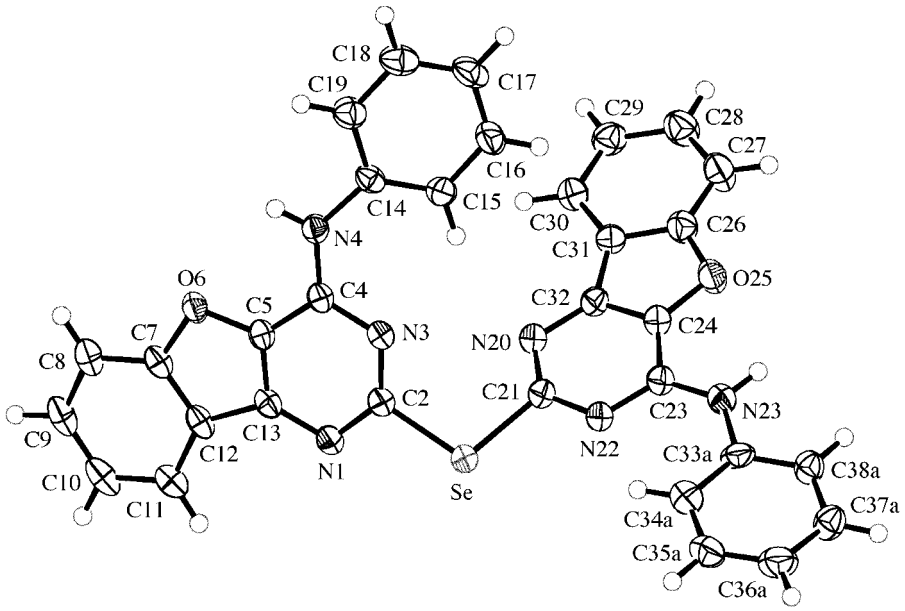
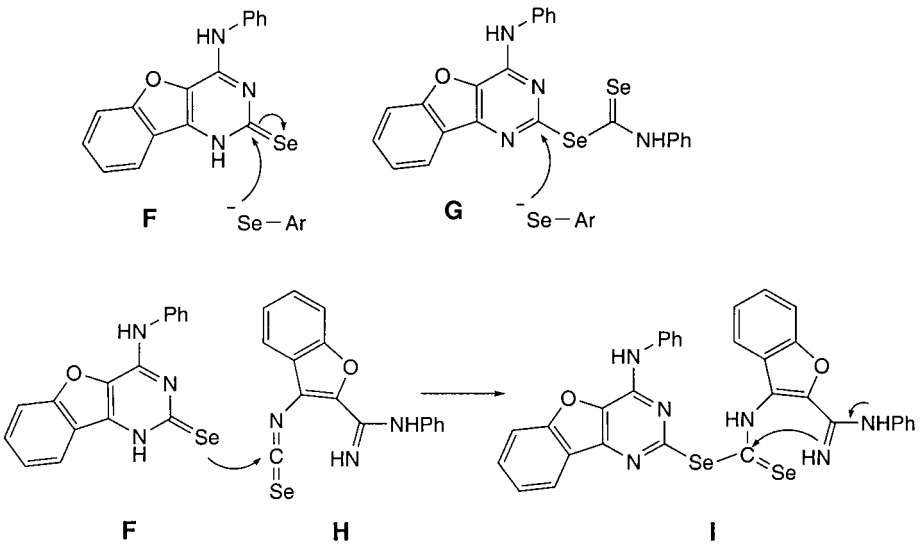


Fig. 3. *ORTEP Plot* [37] *of the molecular structure of* **16** (arbitrary numbering of the atoms, 50% probability ellipsoids, only one conformation of the disordered Ph ring is shown)

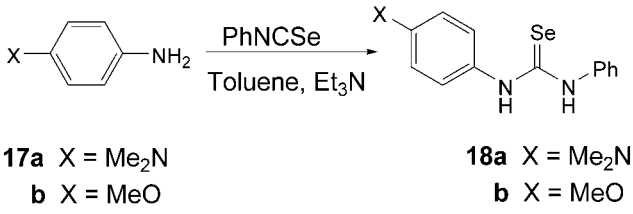


nucleophilic addition of **F** to the isoselenocyanate **H**, which is proposed as an intermediate of the *Dimroth* rearrangement (see **C** in *Scheme 3*), to give **I**, and subsequent cyclization and elimination of H_2Se.

The asymmetric unit of **16** contains one molecule of **16** plus two DMF molecules. The Ph group at N(23) is disordered over two approximately equally occupied orientations, which differ by a rotation of the ring plane by *ca.* 25° about the *ipso*-N–C bond. The mean planes of the fused-ring systems of **16** intersect at an angle of 55.79(5)°. Each NH group forms an intermolecular H-bond with the O-atom of an adjacent DMF molecule.

Finally, phenyl isoselenocyanate (**1a**) has been reacted with 4-(dimethylamino)aniline (**17a**) and 4-methoxyaniline (**17b**) in toluene in the presence of Et_3N. The reactions at room temperature and at 50° gave the corresponding selenourea derivatives **18a** and **18b**, respectively, in good yields (*Scheme 5*). Whereas **18a** is a new compound, **18b** has been prepared previously [44] from the corresponding urea derivative and H_2Se, which is extremely toxic and inconvenient.

Scheme 5



In conclusion, we have shown that the reactions of **8** with phenyl isoseleno- and isothiocyanates (**1a** and **1b**, resp.) proceed in an analogous manner leading to

quinazoline derivatives of type **9** and **10**, respectively. The selones of type **9** can be converted smoothly to diselenides **11** by oxidation with O_2. The analogous oxidation of thione **10** required more-drastic conditions; it was carried out by treatment with I_2. On the other hand, the reaction of **14** with phenyl isoselenocyanate (**1a**) led to a completely different product, *i.e.*, the selenide **16**, compared with the product obtained from the reaction with phenyl isothiocyanate (**1b**). Finally, the preparation of selenoureas of type **18** is more convenient than the method described in the literature.

We thank the analytical units of our institute for spectra and analyses. Financial support of the work by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

Experimental Part

1. *General*. See [29]. IR Spectra in KBr, absorptions in cm^{-1}; NMR spectra in (D_6)DMSO unless otherwise stated, δ in ppm; ^{13}C-signal multiplicity from DEPT spectra; ESI-MS on a *Finnigan TSQ-700* instrument.

2. *Starting Materials*. The phenyl isoselenocyanates **1a**–**1c** were prepared according to the protocol described in [45]. To a stirred soln. of the corresponding *N*-arylformamide (40 mmol) in abs. toluene (100 ml) in an ice bath were added Et_3N (16.2 g, 160 mmol) and Se black powder. Then, phosgene (30 g of a 20% soln. in toluene, 60 mmol) was added slowly over 30 min. An exothermic reaction took place. After complete addition, the suspension was heated under reflux for 8–10 h (TLC control). The mixture was filtered and washed with several portions of toluene, then the filtrate was concentrated and chromatographed (SiO_2; hexane).

Phenyl Isoselenocyanate (**1a**) [45]: from 4.84 g (40 mmol) of *N*-phenylformamide. Yield: 3.24 g (45%). *3-Aminobenzofuran-2-carbonitrile* (**14**) was prepared according to the protocol described in [42]. ^{1}H-NMR ((D_6)DMSO): 7.92 (*d*-like, 1 arom. H); 7.55–7.46 (*m*, 2 arom. H); 7.34–7.29 (*t*-like, 1 arom. H); 6.64 (*s*, NH_2). ^{13}C-NMR ((D_6)DMSO): 154.1, 142.4, 120.9, 114.3, 106.4 (5*s*, 4 arom. C, CN); 129.1, 122.6, 121.2, 111.7 (4*d*, 4 arom. CH).

3. *Synthesis of 4-(Phenylamino)quinazoline-2(1*H*)-selones* **9**. 3.1. *4-(Phenylamino)quinazoline-2(1*H*)-selone* (**9a**). Freshly prepared **1a** (0.6 g, 3.30 mmol) was added to a stirred soln. of *2-aminobenzonitrile* (**8a**; 0.39 g, 3.30 mmol) in dry pyridine at r.t., and the mixture was heated to reflux for 2.5 h. The solvent was removed under reduced pressure, the remaining oil was dissolved in MeOH, and yellow-greenish crystals of **9a** formed, which were recrystallized from MeCN. Yield of **9a**: 0.8 g (81.6%). M.p. 225–240° (MeCN). IR: 2962*m*, 1606*s*, 1563*s*, 1521*s*, 1450*s*, 1426*s*, 1375*s*, 1352*s*, 1334*s*, 1279*s*, 1249*s*, 1183*s*, 1129*m*, 1080*m*. ^{1}H-NMR ((D_6)DMSO): 13.19, 10.13 (2*s*, 2 NH); 8.42 (*d*, $J = 8.1$, 1 arom. H); 7.89–7.21 (*m*, 8 arom. H). 1D-NOESY: Irradiation of H–C(8) increased the intensity of the peak of H–N(1), and irradiation of H–C(5) increased the intensities of the signals of NH and the *ortho*-H-atoms of the PhN group. ^{13}C-NMR ((D_6)DMSO): 177.5 (*s*, SeC); 153.1 (*s*, C(4)); 141.3, 137.9, 110.4 (3*s*, 3 arom. C); 134.5, 128.4, 124.9, 124.2, 123.8, 123.2, 115.8 (7*d*, 9 arom. CH). ESI-MS: 324 (100, $[M+Na]^+$). Anal. calc. for $C_{14}H_{11}N_3Se$ (300.22): C 56.01, H 3.69, N 14.00; found: C 55.80, H 3.84, N 14.22.

3.2. *7-Methyl-4-(phenylamino)quinazoline-2(1*H*)-selone* (**9b**). The reaction was performed as described in *Sect. 3.1* with *2-amino-4-methylbenzonitrile* (**8b**; 0.44 g, 3.30 mmol) and **1a** (0.6 g, 3.30 mmol). Yield of **9b**: 0.7 g (49.3%). M.p. 217.0–219.0° (MeOH). Pale yellow crystals. IR: 3404*w*, 3075*m*, 3021*m*, 2957*m*, 2915*m*, 2860*m*, 1625*s*, 1604*s*, 1567*s*, 1536*s*, 1493*s*, 1448*s*, 1398*m*, 1370*s*, 1342*s*, 1282*s*, 1251*m*, 1226*m*, 1187*s*, 1146*m*, 1101*w*, 1079*m*. ^{1}H-NMR ((D_6)DMSO): 13.10, 10.04 (2*s*, 2 NH); 8.30 (*d*, $J = 8.3$, 1 arom. H); 7.89 (*d*, $J = 7.9$, 2 arom. H); 7.46–7.20 (*m*, 6 arom. H); 2.43 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 177.4 (*s*, SeC); 153.1 (*s*, C(4)); 145.3, 141.5, 138.1, 108.4 (4*s*, 4 arom. C); 128.4, 125.7, 124.8, 123.7, 123.1, 115.3 (6*d*, 8 arom. CH); 21.5 (*q*, Me). CI-MS: 316 (84, $[M+1]^+$). Anal. calc. for $C_{15}H_{13}N_3Se$ (314.24): C 57.33, H 4.17, N 13.37; found: C 56.29, H 4.14, N 12.91.

3.3. *7-Chloro-4-(phenylamino)quinazoline-2(1*H*)-selone* (**9c**). The reaction was performed as described in *Sect. 3.1* with *2-amino-4-chlorobenzonitrile* (**8c**; 0.84 g, 5.50 mmol) and **1a** (1.00 g (5.50 mmol). Yield of **9c**: 0.7 g (38.3%). M.p. 192.1–194.0° (MeOH). Brownish crystals. IR: 3065*m*, 3014*m*, 2899*m*, 1606*s*, 1557*s*, 1528*s*, 1484*s*, 1448*s*, 1393*s*, 1353*s*, 1306*m*, 1289*m*, 1273*m*, 1235*m*, 1180*s*, 1145*m*, 1095*m*, 1071*m*, 1030*w*. ^{1}H-NMR ((D_6)DMSO): 13.18, 10.22 (2*s*, 2 NH); 8.45 (*d*, $J = 8.8$, 1 arom. H); 7.86 (*d*-like, 2 arom. H); 7.80–7.09 (*m*, 5 arom. H). ^{13}C-NMR ((D_6)DMSO): 178.5 (*s*, SeC); 152.6 (*s*, C(4)); 142.2, 139.1, 137.8, 109.4 (4*s*, 4 arom. C); 128.5, 126.2, 125.1, 124.3, 123.2, 115.0 (6*d*, 8 arom. CH).

4. *Synthesis of 4-(Phenylamino)quinazoline-2(1*H*)-thione* (**10**). The reaction was performed as described in *Sect. 3.1* with **8a** (0.87 g, 7.40 mmol) and **1b** (1.00 g, 7.40 mmol). Yield of **10**: 1.46 g (78.0%). M.p. 243.0–244.0°

(MeCN). Yellowish crystals. IR: 3035*m*, 1622*s*, 1607*s*, 1528*s*, 1493*s*, 1451*s*, 1425*m*, 1353*s*, 1335*s*, 1281*m*, 1188*s*, 1160*m*, 1132*m*, 1087*m*. ^{1}H-NMR ((D$_6$)DMSO): 12.72, 10.00 (2*s*, 2 NH); 8.41 (*d*, *J* = 8.2, 1 arom. H); 7.90–7.19 (*m*, 8 arom. H). ^{13}C-NMR ((D$_6$)DMSO): 180.2 (*s*, CS); 154.5 (*s*, C(4)); 141.2, 138.1, 110.0 (3*s*, 3 arom. C); 134.3, 128.3, 124.7, 123.6, 123.4, 123.2, 115.5 (7*d*, 9 arom. CH). ESI-MS: 254 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{11}N_3S$ (253.32): C 66.38, H 4.38, N 16.59; found: C 66.03, H 4.36, N 17.25.

5. *Synthesis of Bis[4-(phenylamino)quinazolin-2-yl] Diselenides* **11**. 5.1. *Bis[4-(phenylamino)quinazolin-2-yl] Diselenide* (**11a**). A soln. of **9a** (0.6 g, 2.0 mmol) in MeCN (15–20 ml) was concentrated a little and allowed to stand at r.t. for several h. Pale-yellow crystals of **11a** formed, and they were separated by filtration: 0.54 g (90.0%) of **11a**. M.p. 158.0–158.5°. IR: 3624*w*, 3423*w*, 3374*m*, 3100*w*, 3055*m*, 1617*s*, 1602*s*, 1560*s*, 1518*s*, 1488*s*, 1447*s*, 1440*s*, 1400*s*, 1358*m*, 1339*s*, 1312*m*, 1299*m*, 1280*s*, 1246*m*, 1193*s*, 1153*m*, 1124*m*, 1112*w*, 1081*m*. ^{1}H-NMR ((D$_6$)DMSO): 9.85 (*s*, 2 NH); 8.52 (*d*, *J* = 8.0, 1 arom. H); 7.94–6.90 (*m*, 16 arom. H). ^{13}C-NMR ((D$_6$)DMSO): 161.3, 157.1, 150.3, 138.5, 113.3 (5*s*, 10 arom. C); 133.6, 128.0, 126.5, 125.6, 123.5, 123.3, 121.8 (7*d*, 18 arom. CH). ESI-MS: 601 (100, $[M+1]^+$). Anal. calc. for $C_{28}H_{20}N_6Se_2$ (598.42): C 56.20, H 3.37, N 14.04; found: C 56.00, H 3.50, N 14.25.

Suitable crystals for an X-ray crystal-structure determination of **11a** were obtained from MeOH. During attempts to grow crystals of **9a**, one crystal of the triselenide **13** with m.p. 114.1–115.2° was obtained from MeCN.

5.2. *Bis[4-[(4-methylphenyl)amino]quinazolin-2-yl] Diselenide* (**11b**). O$_2$ was bubbled through a soln. of **9b** (0.3 g, 95 mmol) in pyridine (10–15 ml) for 2 h. The solvent was removed *i.v.*, and the remaining oil was treated with MeOH to give pale-yellow crystals of **11b**. Yield: 0.2 g (66.0%). M.p. 222.2–224.1° (MeOH). Pale-yellow crystals. IR: 3628*m*, 3427*m*, 3320*m*, 3050*w*, 2914*w*, 1622*s*, 1601*m*, 1560*s*, 1514*s*, 1488*s*, 1447*s*, 1406*s*, 1341*m*, 1310*m*, 1296*m*, 1283*s*, 1251*m*, 1229*m*, 1203*m*, 1135*w*, 1081*m*. ^{1}H-NMR ((D$_6$)DMSO): 9.77 (*s*, 2 NH); 8.41 (*d*, *J* = 8.5, 2 arom. H); 7.95 (*d*, *J* = 7.7, 4 arom. H); 7.52–6.91 (*m*, 12 arom. H); 2.49 (*s*, 2 Me). ^{13}C-NMR ((D$_6$)DMSO): 161.2, 157.0, 150.5, 144.0, 138.7, 111.2 (6*s*, 12 arom. C); 128.0, 127.3, 125.8, 123.4, 123.0, 121.6 (6*d*, 16 arom. CH); 21.2 (*q*, 2 Me). ESI-MS: 629 (100, $[M+1]^+$).

6. *Synthesis of Bis[4-(phenylamino)quinazolin-2-yl] Disulfide* (**12**). To a soln. of **10** (1.0 g, 3.95 mmol) in pyridine (20–25 ml) was added 0.55 equiv. of I$_2$, and the mixture was stirred at r.t. for 1 h. The soln. was poured into H$_2$O, extracted with CH$_2$Cl$_2$, and the org. layer *1* was separated. The aq. layer was mixed with NaHCO$_3$ and extracted again with CH$_2$Cl$_2$, and the org. layer *2* was separated. The solvent of org. layer *1* was evaporated *i.v.* The residue was treated with an aq. soln. of Na$_2$S$_2$O$_3$ and extracted with CH$_2$Cl$_2$. This org. layer was combined with layer *2*, and the soln. was concentrated *i.v.* Pale-yellow crystals of **12** formed. Yield: 0.71 g (71.3%). M.p. 89.1–90.1° (CH$_2$Cl$_2$). IR: 3745*w*, 3422*m*, 3059*w*, 2924*w*, 1616*s*, 1601*s*, 1563*s*, 1520*s*, 1490*s*, 1448*s*, 1406*s*, 1364*m*, 1339*m*, 1307*m*, 1283*s*, 1249*m*, 1194*m*, 1127*w*, 1081*m*, 1031*w*. ^{1}H-NMR ((D$_6$)DMSO): 9.92 (*s*, 2 NH); 8.55 (*d*, *J* = 8.2, 2 arom. H); 7.90–6.92 (*m*, 16 arom. H). ^{13}C-NMR ((D$_6$)DMSO): 164.5, 157.4, 150.3, 138.5, 113.3 (5*s*, 10 arom. C); 133.6, 128.0, 126.5, 125.4, 123.4, 123.2, 121.6 (7*d*, 18 arom. CH). ESI-MS: 505 (100, $[M+1]^+$). Anal. calc. for $C_{28}H_{20}N_6S_2$ (504.63): C 66.64, H 3.99, N 16.65; found: C 65.77, H 4.06, N 16.53.

7. *Synthesis of Bis[4-(phenylamino)benzofuro[3,2-*d*]pyrimidin-2-yl] Selenide* (**16**). The reaction was carried out as described in *Sect. 3.1* with *3-amino[1]benzofuran-2-carbonitrile* (**14**, 0.58 g, 3.67 mmol) and **1a** (0.6 g, 3.30 mmol). Yield of **16**: 0.3 g (27.3%). M.p. 158.0–158.2° (MeCN). Yellowish crystals. IR: 3408*m*, 3347*m*, 3056*m*, 2923*w*, 2852*w*, 2253*w*, 1634*s*, 1613*s*, 1581*s*, 1563*s*, 1514*s*, 1497*s*, 1461*m*, 1437*s*, 1382*m*, 1332*m*, 1299*m*, 1284*s*, 1267*s*, 1223*m*, 1200*m*, 1145*m*, 1133*m*, 1095*m*, 1079*w*, 1031*w*, 1010*w*. ^{1}H-NMR ((D$_6$)DMSO): 10.29 (*s*, 2 PhNH); 8.14 (*d*, *J* = 7.8, 2 arom. H); 7.91–6.81 (*m*, 18 arom. H). ^{13}C-NMR ((D$_6$)DMSO): 159.5, 156.0, 147.1, 146.3, 138.7, 133.9 (6*s*, 14 arom. C); 130.7, 128.0, 124.3, 122.9, 121.6, 120.2, 112.7 (7*d*, 18 arom. CH). ESI-MS: 601 (100, $[M+1]^+$). Anal. calc. for $C_{32}H_{20}N_6O_2Se$ (599.50): C 64.11, H 3.36, N 14.02; found: C 62.95, H 3.62, N 14.87.

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

8. *Preparation of N,N′-Diarylselenoureas* **18**. 8.1. N-*[4-(Dimethylamino)phenyl]*-N′-*phenylselenourea* (**18a**). To a stirred soln. of 4-(dimethylamino)aniline (0.45 g, 3.30 mmol) in toluene (20–25 ml) at r.t. were added **1a** (0.6 g, 3.30 mmol) and 3 drops of Et$_3$N. The mixture was stirred for 10 min at r.t. and 20 min at 50°. The soln. was concentrated *i.v.*, and the product precipitated was isolated by filtration. Yield of **18a**: 0.85 g (81.0%). M.p. 138.0–138.5° (toluene). Grey crystals. IR: 3567*w*, 3167*s*, 3000*s*, 2799*m*, 2037*w*, 1948*w*, 1897*w*, 1614*m*, 1599*m*, 1591*m*, 1578*m*, 1552*s*, 1494*s*, 1450*m*, 1323*s*, 1226*s*, 1188*m*, 1167*m*, 1131*m*. ^{1}H-NMR (CDCl$_3$): 8.70–7.80 (br. *s*, 2 NH); 7.35–6.64 (*m*, 7 arom. H); 6.62 (*AA′BB′*, *J* = 1.9, 2 arom. H); 2.90 (*s*, 2 Me). ^{13}C-NMR (CDCl$_3$)[3]):

[3]) Two *singlets* for arom. C are missing or overlap with other signals.

179.0 (*s*, SeC); 150.0 (*s*, 1 arom. C); 129.1, 127.3, 127.0, 125.6, 112.7 (5*d*, 9 arom. CH); 40.3 (*q*, 2 Me). ESI-MS: 320 (100, $[M+1]^+$). Anal. calc. for $C_{15}H_{17}N_3Se$ (318.28): C 56.61, H 5.38, N 13.20; found: C 56.48, H 5.42, N 13.33.

8.2. N-*(4-Methoxyphenyl)*-N′-*phenylselenourea* (**18b**) [44]. In analogy to *Sect. 8.1*, 4-methoxyaniline (0.2 g, 1.65 mmol) and **1a** (0.3 g, 1.65 mmol) were reacted at r.t. for 2 h. Yield of **18b**: 0.3 g (60.0%). M.p. 176.0–176.5° (MeCN). Grey crystals. IR: 3457*m*, 3175*s*, 3035*s*, 3006*s*, 2838*m*, 2058*w*, 1957*w*, 1912*w*, 1610*m*, 1599*m*, 1589*m*, 1556*s*, 1527*s*, 1506*s*, 1467*m*, 1450*m*, 1417*m*, 1337*s*, 1296*s*, 1249*s*, 1220*m*, 1182*m*, 1169*m*, 1102*m*, 1034*s*. ^{1}H-NMR ((D$_6$)DMSO): 9.93 (br. *s*, 2 NH); 7.41–6.92 (*m*, 7 arom. H); 6.89 (*AA′BB′*, *J* = 7.2, 2 arom. H); 3.75 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 178.6 (*s*, SeC); 157.0, 139.6, 132.3 (3*s*, 3 arom. C); 128.3, 126.7, 125.0, 124.7, 113.7 (5*d*, 9 arom. CH); 55.1 (*q*, Me). ESI-MS: 305 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{14}N_2OSe$ (305.23): C 55.09, H 4.62, N 9.18; found: C 54.92, H 4.74, N 9.17.

9. *X-Ray Crystal-Structure Determination of* **10**, **11a**, **13**, *and* **16** (see *Table* and *Figs. 1–3*)[4]). All measurements were performed on a *Nonius KappaCCD* diffractometer [46] with graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1–3*. Data reduction was performed with *HKL Denzo* and *Scalepack* [47]. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections were applied (multi-scan method [48] for **10** and a numerical correction [49] for **11a**, **13**, and **16**). Each structure was solved by direct methods with SHELXS97 [50] in the cases of **10**, **13**, and **16**, and SIR92 [51] in the case of **11a**. The asymmetric unit in the structure of **10** contains one molecule of the thione plus one MeOH molecule, while that of **11a** contains one diselenide molecule plus two MeOH molecules, and that of **13** contains one half of the triselenide molecule, which sits across a two-fold axis, plus one H_2O molecule. The asymmetric unit of **16** contains one molecule of the selenide plus two molecules of DMF. In addition, the Ph group at N(23) of **16** is disordered over two orientations, which differ by a rotation of the ring plane of *ca.* 25°. Two positions were defined for each atom of this ring, and refinement of constrained site occupation factors for the two orientations yielded a value of 0.51(2) for the major conformation. Bond-length and similarity restraints were applied to all C–C bonds within both orientations of the disordered ring, and neighboring atoms within and between each conformation of the disordered ring were restrained to have similar atomic displacement parameters.

The non-H-atoms in each structure were refined anisotropically. With the exception of the disordered H-atoms at N(23) in **16**, the amine H-atoms, as well as the OH H-atoms of any MeOH or H_2O solvent molecules, were placed in the positions indicated by difference-electron-density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms in each structure were placed in geometrically calculated positions, and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom. Refinement of each structure was carried out on *F* (**10**, **11a**, **13**) or F^2 (**16**) using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_c|)^2$ or $\Sigma w(F_o^2-F_c^2)^2$, resp. A correction for secondary extinction was applied in the case of **11a**. For **13**, refinement of the absolute structure parameter [52] yielded a value of $-0.010(9)$, which confidently confirms that the refined model represents the true absolute structure. Neutral-atom-scattering factors for non-H-atoms were taken from [53a], and the scattering factors for H-atoms were taken from [54]. Anomalous dispersion effects were included in F_c [55]; the values for f' and f'' were those of [53b]. The values of the mass-attenuation coefficients are those of [53c]. All calculations for **10**, **11a**, and **13** were performed using the teXsan crystallographic software package [56], while those for **16** employed the SHELXL97 program [57].

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[4]) CCDC-230431-CCDC-230434 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk)).

Table. *Crystallographic Data of* **10**, **11a**, **13**, *and* **16**

	10	**11a**	**13**	**16**
Crystallized from	MeOH	MeOH	MeCN	DMF
Empirical formula	$C_{14}H_{11}N_3S \cdot CH_4O$	$C_{28}H_{20}N_6Se_2 \cdot 2\ CH_4O$	$C_{28}H_{20}N_6Se_3 \cdot 2\ H_2O$	$C_{32}H_{20}N_6O_2Se \cdot 2\ C_3H_7NO$
Formula weight [g mol^{-1}]	285.36	662.39	713.24	745.64
Crystal color, habit	colorless, plate	pale-yellow, prism	yellow, needle	yellow, prism
Crystal dimensions [mm]	$0.02 \times 0.12 \times 0.22$	$0.10 \times 0.18 \times 0.25$	$0.05 \times 0.10 \times 0.25$	$0.10 \times 0.12 \times 0.20$
Temp. [K]	160(1)	160(1)	160(1)	160(1)
Crystal system	triclinic	monoclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12$	$P\bar{1}$
Z	2	4	2	2
Reflections for cell determination	20094	130251	23666	75744
2θ Range for cell determination [°]	4 – 52	4 – 55	4 – 60	4 – 60
Unit-cell parameters a [Å]	6.8860(1)	12.5727(2)	17.3474(2)	7.6275(1)
b [Å]	9.9602(2)	13.8628(2)	18.1483(3)	11.4277(1)
c [Å]	10.1304(2)	16.7361(3)	4.3127(1)	20.8212(3)
α [°]	88.9010(9)	90	90	74.2308(5)
β [°]	85.286(1)	102.2947(6)	90	83.6393(6)
γ [°]	85.2725(8)	90	90	76.9206(6)
V [Å^3]	690.04(2)	2850.08(8)	1357.75(4)	1698.91(4)
D_x [g cm^{-3}]	1.373	1.544	1.744	1.457
μ(MoK_α) [mm^{-1}]	0.233	2.632	4.100	1.160
Scan type	ω	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	52	55	60	60
Transmission factors (min; max)	0.914; 1.000	0.593; 0.789	0.471; 0.802	0.830; 0.905
Total reflections measured	11349	64492	31729	47492
Symmetry-independent reflections	2680	6525	3957	9887
Reflections with $I > 2\sigma(I)$	2126	4892	3422	6807
Parameters refined; restraints	193; 0	378; 0	190; 0	523; 206
$R(F)$ [$I > 2\sigma(I)$ reflections]	0.0432	0.0431	0.0291	0.0435
$wR(F)$ [$I > 2\sigma(I)$ reflections]	0.0448	0.0452	0.0291	0.1142 (on F^2, all reflections)
Weights: p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.005	0.015	0.015	[a])
Goodness of fit	1.955	1.755	1.147	1.039
Secondary extinction coefficient	–	$2.2(7) \times 10^{-7}$	–	–
Final Δ_{max}/σ	0.0001	0.0005	0.001	0.001
$\Delta\rho$ (max; min) [e · Å^{-3}]	0.24; −0.23	0.76; −0.54	0.57; −0.43	0.58; −0.74

[a]) $w = [\sigma^2(F_o^2) + (0.0526P)^2 + 0.4229P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

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