Synthesis of 1,3-Selenazol-2(3*H*)-imines

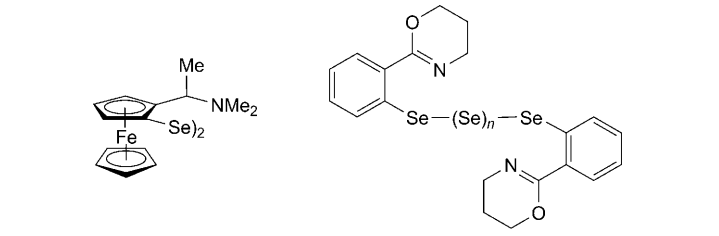
by **Plamen K. Atanassov**[1]), **Anthony Linden**, and **Heinz Heimgartner***

Organisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (phone: +41-44-635 4282; fax: +41-44-635 6812; e-mail: heimgart@oci.uzh.ch)

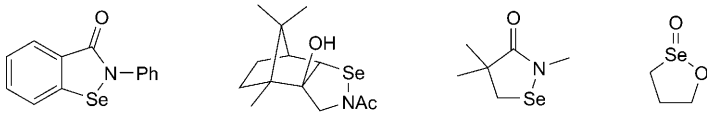
Dedicated to Prof. *Ludmila L. Rodina*, Saint Petersburg, on the occasion of her 70th birthday

The reaction of *N*,*N*′-diarylselenoureas **16** with phenacyl bromide in EtOH under reflux, followed by treatment with NH_3, gave *N*,3-diaryl-4-phenyl-1,3-selenazol-2(3*H*)-imines **13** in high yields (*Scheme 2*). A reaction mechanism *via* formation of the corresponding *Se*-(benzoylmethyl)isoselenoureas **18** and subsequent cyclocondensation is proposed (*Scheme 3*). The *N*,*N*′-diarylselenoureas **16** were conveniently prepared by the reaction of aryl isoselenocyanates **15** with 4-substituted anilines. The structures of **13a** and **13c** were established by X-ray crystallography.

Introduction. – Since the discovery of the importance of Se as a microelement in bacteria and animals [1], and the function of the selenoenzyme glutathione peroxidase (GPx) as an antioxidant [2], the interest in organoselenium compounds has increased significantly. As a result, a large series of organoselenium compounds was prepared as GPx mimics, *e.g.*, diorgano di- and triselenides **1** and **2** [3–5], and selenaheterocycles **3**–**6** [6][7]. In recent years, isoselenocyanates have been shown to be useful building blocks for the synthesis of Se-containing heterocycles [8].



1 **2** *n* = 0, 1



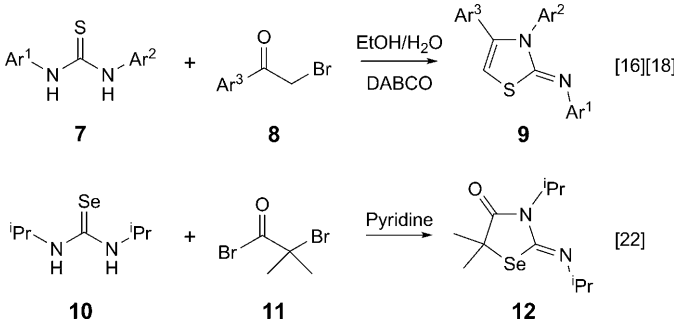
3 **4** **5** **6**

As continuation of our studies toward the use of isoselenocyanates in the synthesis of 1,3-selenazole derivatives [9–14] and with the aim of preparing 1,3-selenazol-

[1]) Postdoctoral stay at the University of Zürich (04.–12.2004).

2(3*H*)-imines, we investigated the reaction of selenourea derivatives, which are easily accessible from isoselenocyanates, with phenacyl bromide. Whereas the analogous synthesis of 1,3-thiazol-2(3*H*)-imines **9** *via* the reaction of thioureas **7** with phenacyl bromides **8**, *i.e.*, the *Hantzsch* condensation reaction [15], is well-known [16–21] (*Scheme 1*), no synthesis of the corresponding 1,3-selenazol-2(3*H*)-imines has been reported so far.

Scheme 1



Very recently, *Koketsu et al.* and other groups reported on the synthesis of some 1,3-selenazolidine-2-imines [22–25]. For example, *N*,*N*′-diisopropylselenourea (**10**) and 2-bromo-2-methylpropanoyl bromide (**11**) in pyridine led to the 2-imino-1,3-selenazolidin-4-one **12**, the structure of which has been determined by X-ray crystallography [22] (*Scheme 1*).

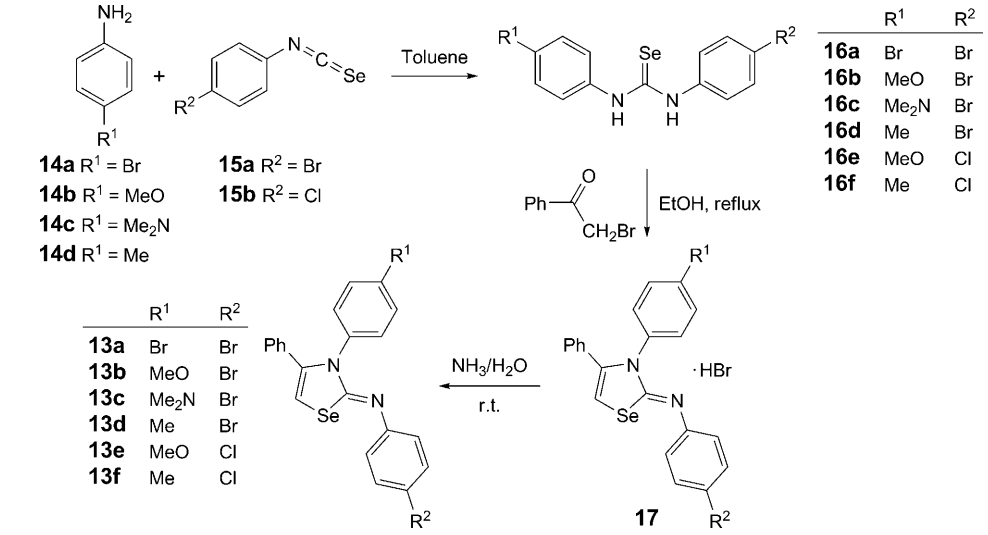
Here, we describe the synthesis of some *N*,3-diaryl-4-phenyl-1,3-selenazol-2(3*H*)-imines **13** in a two step reaction from anilines **14**, aryl isoselenocyanates **15**, and phenacyl bromide.

Results and Discussion. – The selenoureas **16** were prepared conveniently according to the protocol reported in [26]. The reaction of 4-bromophenyl and 4-chlorophenyl isoselenocyanate (**15a** and **15b**, resp.) with 4-substituted anilines **14** in tolouene in the presence of a catalytic amount of Et_3N gave **16a**–**16f** in high yields as crystalline materials (*Scheme 2*). Then, the solution of equimolar amounts of **16** and phenacyl bromide in EtOH was heated to reflux for 2 h. The cooled mixture was poured into H_2O and treated with aqueous NH_3 to convert the formed hydrobromides **17** to the free 1,3-selenazol-2(3*H*)-imines **13** (*Scheme 2*). The products were isolated in good yield as colorless solids.

The structures of the products were determined on the basis of the spectroscopic and analytical data, and, in the cases of **13a** and **13c**, they were established by X-ray crystallography (*Fig.*). In both cases, the five-membered heterocycle is planar, but none of the aryl rings is coplanar with it. In **13c**, the 4-(dimethylamino)phenyl residue is attached to the N-atom of the 1,3-thiazole ring, and the 4-bromophenyl moiety is located at the imine N-atom.

According to the NMR spectra, only one product was formed in the reactions with **16a**–**16c** and **16e**, *i.e.*, the formation of **13b**, **13c**, and **13e** occurred regioselectively. On the other hand, the products of the reaction with **16d** and **16f** consisted of a *ca.* 4:1

Scheme 2



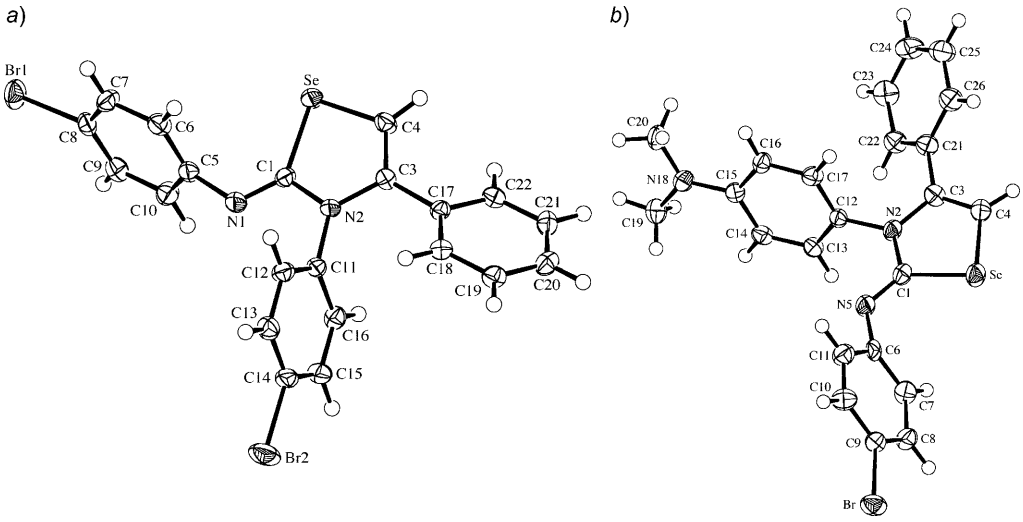
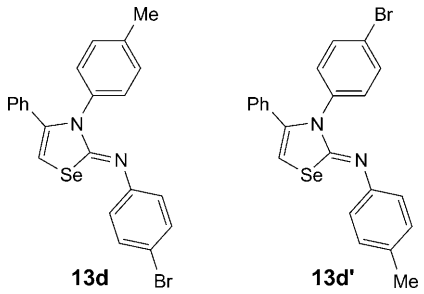


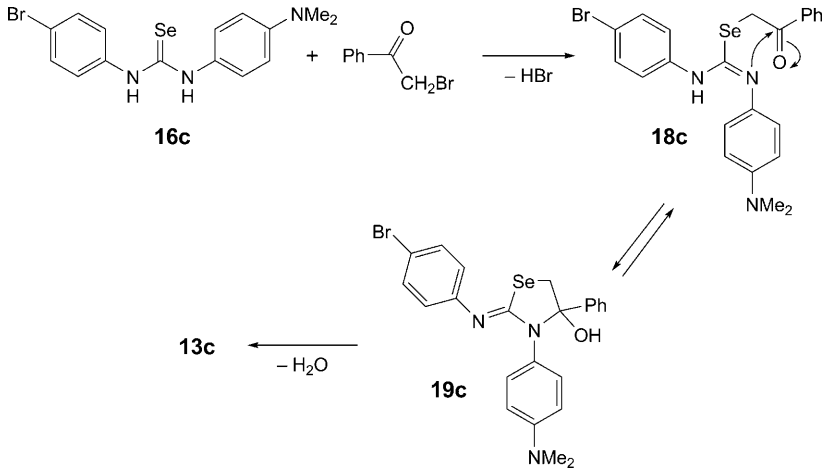
Figure. *ORTEP Plot* [27] *of the molecular structure of* **13a** *and* **13c** (50% probability ellipsoids, arbitrary numbering of the atoms)

mixture of two isomeric compounds. For example, the ^{1}H-NMR spectrum of the product from **16d** and phenacyl bromide showed *singlet*s at 6.37 and 6.41 ppm for H–C(5), and 2.27 and 2.32 ppm for Me, each with an intensity ratio of *ca.* 4 : 1. We assigned the structures **13d** and **13d′** to these products.

Based on the presented results and in analogy to the *Hantzsch* thiazole synthesis, we propose the following reaction mechanism (*Scheme 3*): nucleophilic substitution of Br in phenacyl bromide by the Se-atom of selenourea **16** leads to the isoselenourea



Scheme 3



derivative **18**, which subsequently undergoes a cyclocondensation to give the hydrobromide of **13** (*cf.* [17]). The plausible intermediate is **19**, formed *via* nucleophilic addition of an N-atom of **18** onto the C=O group.

In the case of **18c**, the cyclization occurs selectively *via* the more nucleophilic N-atom, bearing the 4-(dimethylamino)phenyl residue. The same selectivity was observed in the cases of the reactions with **16b** and **16e** with a 4-methoxyphenyl substituent. The formation of two isomers of type **13d** and **13d'** in the reaction with **16d** and **16f**, respectively, which bear a 4-methylphenyl substituent in addition to a 4-bromo- or 4-chlorophenyl residue, can be explained with the smaller difference of the nucleophilicity of the two N-atoms due to the lower electron-donating properties of the Me group in comparison with the Me_2N and MeO groups.

In conclusion, a convenient synthesis of the little known 1,3-selenazol-2(3*H*)-imines from diarylselenoureas and phenacyl bromide was developed. This approach can easily be applied for the preparation of differently substituted analogues.

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 [28]. M.p.: *Mettler-FP-5* or *Büchi B-450* apparatus; uncorrected. IR Spectra: *Perkin-Elmer-781* or *Perkin-Elmer-1600-FT-IR* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: *Bruker-AC-300* or *Bruker-ARX-300* instrument (300 and 75.5 MHz, resp.), in (D_6)DMSO or $CDCl_3$; multiplicity of C-atoms from DEPT spectra. MS: *Finnigan MAT-90* or *Finnigan SSQ-700* instrument (CI (NH_3) or ESI). Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-chemischen Instituts der Universität Zürich.

2. *Starting Materials. 4-Bromophenyl isoselenocyanate* (**15a**) and *4-chlorophenyl isoselenocyanate* (**15b**) were prepared according to the protocol described in [29], and *N,N′*-diarylselenoureas **16** were prepared according to [26]. All other chemicals were commercially available.

3. *Synthesis of* N,N′-*Selenoureas* **16**. 3.1. N,N′-*Bis(4-bromophenyl)selenourea* (**16a**) [30]. From 1.05 g (4 mmol) of **15a** and 0.69 g (4 mmol) of *4-bromoaniline* (**14a**): 1.6 g (92%) of **16a**. M.p. 222.6–224.0° (toluene). Creamy solid. IR: 3175*s*, 3021*s*, 2998*s*, 2832*m*, 1580*m*, 1552*s*, 1524*s*, 1485*s*, 1401*m*, 1333*s*, 1310*s*, 1271*m*, 1254*m*, 1236*m*, 1217*m*, 1171*w*, 1094*w*, 1072*s*, 1016*s*, 920*m*, 851*m*, 827*s*. ^{1}H-NMR ((D_6)DMSO): 10.25 (*s*, 2 NH); 7.52, 7.38 (*AA′BB′*, J_{AB} = 8.8, 8 arom. H). ^{13}C-NMR ((D_6)DMSO): 179.1 (*s*, CSe); 138.9, 117.5 (2*s*, 4 arom. C); 131.3, 126.7 (2*d*, 8 arom. CH). CI-MS: 437 (18), 435 (38, $[M+1]^+$), 433 (30), 431 (12), 357 (41), 356 (17), 355 (100), 354 (17), 352 (80). Anal. calc. for $C_{13}H_{10}Br_2N_2Se$ (433.00): C 36.06, H 2.33, N 6.47; found: C 35.52, H 2.31, N 6.39.

3.2. N-*(4-Bromophenyl)*-N′-*(4-methoxyphenyl)selenourea* (**16b**). From 0.5 g (1.9 mmol) of **15a** and 0.23 g (1.9 mmol) of *4-methoxyaniline* (**14b**): 0.57 g (80.3%) of **16b**. M.p. 188.8–190.3° (CH_2Cl_2/hexane). IR: 3175*s*, 3000*s*, 2836*m*, 1608*m*, 1587*w*, 1553*s*, 1527*m*, 1505*s*, 1482*m*, 1463*m*, 1339*s*, 1297*s*, 1247*s*, 1218*m*, 1180*m*, 1166*m*, 1103*m*, 1068*m*, 1031*m*, 1015*m*, 921*w*, 851*w*, 833*s*. ^{1}H-NMR ((D_6)DMSO): 10.08, 9.94 (2*s*, 2 NH); 7.50, 7.37 (*AA′BB′*, J_{AB} = 8.8, 4 arom. H); 7.26, 6.91 (*AA′BB′*, J_{AB} = 8.9, 4 arom. H); 3.75 (*s*, MeO). ^{13}C-NMR ((D_6)DMSO): 178.8 (*s*, CSe); 157.0, 139.2, 132.1, 117.2 (4*s*, 4 arom. C); 131.1, 126.8, 126.6, 113.7 (4*d*, 8 arom. CH); 55.1 (*q*, MeO). CI-MS: 387 (3), 385 (4, $[M+1]^+$), 383 (2), 307 (41), 306 (17), 305 (100), 304 (13), 303 (60). Anal. calc. for $C_{14}H_{13}BrN_2OSe$ (384.13): C 43.77, H 3.41, N 7.29; found: C 43.83, H 3.50, N 7.34.

3.3. N-*(4-Bromophenyl)*-N′-*[4-(dimethylamino)phenyl]selenourea* (**16c**). From 1.0 g (3.83 mmol) of **15a** and 0.52 g (3.82 mmol) of *4-(dimethylamino)aniline* (**14c**): 1.3 g (86%) of **16c**. M.p. 171.3–174.0° (CH_2Cl_2/hexane). IR: 3172*s*, 3004*s*, 2884*m*, 2842*m*, 2800*m*, l611*m*, 1575*w*, 1551*s*, 1531*s*, 1515*s*, 1483*m*, 1444*w*, 1397*w*, 1329*s*, 1309*s*, 1247*m*, 1224*m*, 1184*w*, 1165*w*, 1128*w*, 1097*w*, 1064*m*, 1012*m*, 945*m*, 920*m*, 819*s*. ^{1}H-NMR ((D_6)DMSO): 10.01, 9.74 (2*s*, 2 NH); 7.48, 7.37 (*AA′BB′*, J_{AB} = 8.9, 4 arom. H); 7.13, 6.69 (*AA′BB′*, J_{AB} = 8.9, 4 arom. H); 2.89 (*s*, 2 Me). ^{13}C-NMR ((D_6)DMSO): 178.2 (*s*, CSe); 148.6, 139.4, 127.9, 117.1 (4*s*, 4 arom. C); 131.0, 126.9, 126.1, 112.2 (4*d*, 8 arom. CH); 40.1 (*q*, 2 Me). ESI-MS: 400 (100), 398 (86, $[M+1]^+$), 396 (48). Anal. calc. for $C_{15}H_{16}BrN_3Se$ (397.17): C 45.36, H 4.06, N 10.58; found: C 45.49, H 4.12, N 10.60.

3.4. N-*(4-Bromophenyl)*-N′-*(4-methylphenyl)selenourea* (**16d**). From 0.5 g (1.9 mmol) of **15a** and 0.2 g (1.9 mmol) of *4-methylaniline* (**14d**): 0.6 g (88.2%) of **16d**. M.p. 195.2–197.0 (CH_2Cl_2/hexane). IR: 3167*s*, 3001*s*, 2919*w*, 2832*w*, 1581*m*, 1551*s*, 1530*m*, 1506*m*, 1484*s*, 1398*w*, 1380*w*, 1335*s*, 1238*m*, 1219*m*, 1175*w*, 1106*w*, 1098*w*, 1068*m*, 1014*s*, 921*w*, 844*w*, 822*s*. ^{1}H-NMR ((D_6)DMSO): 10.25, 10.10 (2*s*, 2 NH); 7.58, 7.45 (*AA′BB′*, J_{AB} = 8.8, 4 arom. H); 7.33, 7.22 (*AA′BB′*, J_{AB} = 8.3, 4 arom. H); 2.36 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 178.6 (*s*, CSe); 139.2, 136.7, 134.6, 117.2 (4*s*, 4 arom. C); 131.1, 129.0, 126.7, 124.6 (4*d*, 8 arom. CH); 20.4 (*q*, Me). CI-MS: 371 (4), 369 (6, $[M+1]^+$), 367 (3), 291 (37), 290 (16), 289 (100), 288 (14), 287 (66). Anal. calc. for $C_{14}H_{13}BrN_2Se$ (368.13): C 45.68, H, 3.56, N 7.61; found: C 45.60, H 3.64, N 7.60.

3.5. N-*(4-Chlorophenyl)*-N′-*(4-methoxyphenyl)selenourea* (**16e**). From 0.7 g (3.2 mmol) of **15b** and 0.4 g (3.2 mmol) of **14b**: 1.0 g (90.9%) of **16e**. M.p. 187.9–189.1° (CH_2Cl_2/hexane). IR: 3177*s*, 3001*s*, 2836*m*, 1609*m*, 1587*w*, 1554*s*, 1525*m*, 1505*s*, 1486*m*, 1463*m*, 1441*w*, 1401*w*, 1336*s*, 1297*s*, 1248*s*, 1218*m*, 1180*m*, 1166*m*, 1102*m*, 1090*m*, 1031*m*, 1018*m*, 922*w*, 852*w*, 834*s*, 821*m*. ^{1}H-NMR ((D_6)DMSO): 10.07, 9.94 (2*s*, 2 NH); 7.42, 7.38 (*AA′BB′*, J_{AB} = 8.9, 4 arom. H); 7.26, 6.91 (*AA′BB′*, J_{AB} = 8.9, 4 arom. H); 3.75 (*s*, Me). ^{13}C-NMR ((D_6)DMSO): 178.8 (*s*, CSe); 157.0, 138.7, 132.1, 129.0 (4*s*, 4 arom. C); 128.1, 126.6, 126.5, 113.7 (4*d*, 8 arom. CH); 55.1 (*q*, Me). CI-MS: 343 (1), 341 (3, $[M+1]^+$), 339 (1), 263 (14), 262

(11), 261 (73), 260 (18), 259 (100). Anal. calc. for $C_{14}H_{13}ClN_2OSe$ (339.68): C 49.50, H 3.86, N 8.25; found: C 49.68, H 3.97, N 8.32.

3.6. N-*(4-Chlorophenyl)*-N′-*(4-methylphenyl)selenourea* (**16f**). From 0.7 g (3.2 mmol) of **15b** and 0.34 g (3.2 mmol) of **14d**: 0.9 g (88.2%) of **16f**. M.p. 195.2–195.9° (CH_2Cl_2/hexane). IR: 3172*s*, 3002*s*, 2921*m*, 2832*w*, 1584*m*, 1553*s*, 1506*m*, 1489*m*, 1403*w*, 1380*w*, 1332*s*, 1238*m*, 1220*w*, 1175*w*, 1090*s*, 1017*m*, 921*w*, 849*w*, 824*s*. ^{1}H-NMR ((D$_6$)DMSO): 10.42, 10.29 (2*s*, 2 NH); 7.69, 7.62 (*AA′BB′*, J_{AB} = 8.9, 4 arom. H); 7.52, 7.41 (*AA′BB′*, J_{AB} = 8.3, 4 arom. H); 2.54 (*s*, Me). ^{13}C-NMR ((D$_6$)DMSO): 178.7 (*s*, CSe); 138.7, 136.7, 134.6 (3*s*, 4 arom. C); 129.0, 128.2, 126.4, 124.6 (4*d*, 8 arom. CH); 20.4 (*q*, Me). CI-MS: 327 (3), 325 (5, $[M + 1]^+$), 323 (3), 247 (14), 246 (12), 245 (74), 244 (19), 243 (100). Anal. calc. for $C_{14}H_{13}ClN_2Se$ (323.68): C 51.95, H 4.05, N 8.65; found: C 51.99, H 4.09, N 8.75.

4. *Reaction of* N,N′-*Diarylselenoureas* **16** *with Phenacyl Bromide. General Procedure.* Approximately 2.5 ml of abs. EtOH were added to a mixture of equimolecular amounts (1–2 mmol) of **16** and phenacyl bromide. The mixture was stirred for 2 h under reflux. Then, the soln. was cooled to r.t., poured into cold H_2O, and treated with aq. NH_3. The solid obtained was filtered and dried ($MgSO_4$). The mother liquor was concentrated *in vacuo*, MeOH was added, and the white solid formed was again filtered and dried.

4.1. *N,3-Bis(4-bromophenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13a**). From 0.73 g (1.7 mmol) of **16a** and 0.33 g (1.7 mmol) of phenacyl bromide: 0.7 g (77.8%) of **13a**. M.p. 193.1–194.4° ($CHCl_3$/MeOH). White solid. IR: 3121*w*, 3103*w*, 3084*w*, 3055*w*, 1623*s*, 1574*m*, 1556*m*, 1484*m*, 1475*m*, 1445*w*, 1396*w*, 1349*m*, 1298*m*, 1249*m*, 1144*m*, 1093*w*, 1062*m*, 1013*m*, 1004*m*, 919*m*, 868*m*, 825*m*. ^{1}H-NMR ($CDCl_3$): 7.44–7.41 (*m*, 4 arom. H); 7.40–7.22 (*m*, 3 arom. H); 7.21–7.06 (*m*, 4 arom. H); 6.94 (*BB′* of *AA′BB′*, J_{AB} = 8.6, 2 arom. H); 6.43 (*s*, H–C(5)). ^{13}C-NMR ($CDCl_3$): 141.4, 137.5, 132.4, 128.4, 121.8, 117.2 (6*s*, 5 arom. C, C(2), C(4)); 132.8, 132.2, 130.5, 128.61, 128.58, 128.4, 123.2 (7*d*, 13 arom. CH); 98.0 (*d*, C(5)). CI-MS: 539 (7), 538 (12), 537 (52), 536 (27), 535 (100, $[M + 1]^+$), 534 (32), 533 (83), 532 (25), 531 (35), 530 (10). Anal. calc. for $C_{21}H_{14}Br_2N_2Se$ (533.12): C 47.31, H 2.65, N 5.25; found: C 47.12, H 2.80, N 5.24.

Suitable crystals of **13a** for the X-ray crystal structure determination were obtained from Et_2O by slow evaporation of the solvent at 5°.

4.2. N-*(4-Bromophenyl)-3-(4-methoxyphenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13b**). From 0.3 g (0.78 mmol) of **16b**, 0.15 g (0.78 mmol) of phenacyl bromide, and 15–20 ml of EtOH: 0.35 g (92%) of **13b**. M.p. 214.9–215.3° (CH_2Cl_2/MeOH). IR: 3097*w*, 3055*w*, 3010*w*, 2958*w*, 2928*w*, 2901*w*, 2830*w*, 1614*s*, 1602*s*, 1573*s*, 1557*m*, 1509*s*, 1490*w*, 1479*s*, 1462*w*, 1449*w*, 1434*w*, 1347*m*, 1300*m*, 1285*w*, 1248*s*, 1146*s*, 1096*w*, 1067*m*, 1028*m*, 1006*m*, 919*w*, 871*m*, 830*m*. ^{1}H-NMR ($CDCl_3$): 7.41, 6.96 (*AA′,BB′*, J_{AB} = 8.4, 4 arom. H); 7.25–7.08 (*m*, 7 arom. H); 6.80 (*BB′* of *AA′BB′*, J_{AB} = 8.7, 2 arom. H); 6.41 (*s*, H–C(5)); 3.74 (*s*, MeO). ^{13}C-NMR ($CDCl_3$): 158.8, 142.1, 131.1, 116.7 (4*s*, 5 arom. C, C(2), C(4)); 132.6, 129.8, 128.6, 128.3, 128.0, 123.4, 114.3 (7*d*, 13 arom. CH); 97.5 (*d*, C(5)); 55.2 (*q*, MeO). CI-MS: 489 (14), 488 (20), 487 (78), 486 (28), 485 (100, $[M + 1]^+$), 484 (26), 483 (46), 482 (15), 481 (14). Anal. calc. for $C_{22}H_{17}BrN_2OSe$ (484.25): C 54.57, H 3.54, N 5.78; found: C 54.15, H 3.59, N 5.75.

4.3. N-*(4-Bromophenyl)-3-[4-(dimethylamino)phenyl]-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13c**). From 0.6 g (1.5 mmol) of **16c** and 0.3 g (1.5 mmol) of phenacyl bromide: 0.55 g (73.3%) of **13c**. M.p. 209.3–212.5° (CH_2Cl_2/MeOH). IR: 3106*w*, 2889*w*, 2861*w*, 2817*w*, 1608*s*, 1571*s*, 1557*m*, 1528*s*, 1489*m*, 1475*s*, 1443*m*, 1374*w*, 1338*s*, 1316*w*, 1289*m*, 1248*m*, 1232*m*, 1191*w*, 1138*s*, 1062*s*, 1000*m*, 918*w*, 860*m*, 825*m*, 809*m*. ^{1}H-NMR ($CDCl_3$): 7.40, 6.89 (*AA′BB′*, J_{AB} = 8.7, 4 arom. H); 7.26–7.04 (*m*, 7 arom. H); 6.63 (*BB′* of *AA′BB′*, J_{AB} = 8.8, 2 arom. H); 6.29 (*s*, H–C(5)); 2.90 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$): 143.1, 133.9, 123.1, 116.2 (4*s*, 5 arom. C, C(2), C(5)); 133.3, 132.6, 129.5, 128.6, 128.5, 128.0, 123.2 (7*d*, 13 arom. CH); 95.7 (*d*, C(5)); 40.7 (*q*, 2 Me). ESI-MS: 500 (46), 498 (100, $[M + 1]^+$), 496 (40), 494 (24). Anal. calc. for $C_{23}H_{20}BrN_3Se$ (497.29): C 55.55, H 4.05, N 8.45; found: C 55.73, H 4.08, N 8.38.

Suitable crystals of **13c** for the X-ray crystal structure determination were obtained from Et_2O by slow evaporation of the solvent at 5°.

5.4. N-*(4-Bromophenyl)-3-(4-methylphenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13d**) *and 3-(4-Bromophenyl)*-N-*(4-methylphenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13d′**). From 0.3 g (0.81 mmol) of **16d** and 0.162 g (0.81 mmol) of phenacyl bromide: 0.3 g (78.9%) of **13d**. M.p. 193.4–193.8° (CH_2C1_2/MeOH). IR: 3103*w*, 3051*w*, 3032*w*, 2918*w*, 1626*s*, 1604*s*, 1574*m*, 1508*m*, 1488*m*, 1478*m*, 1441*w*, 1350*m*, 1292*m*, 1246*m*, 1141*m*, 1065*m*, 1028*w*, 1006*m*, 916*m*, 868*m*, 826*m*. ^{1}H-NMR ($CDCl_3$; two isomers 4:1):

7.40, 6.92 ($AA'BB'$, J_{AB} = 8.6, 4 arom. H); 7.30–7.05 (*m*, 9 arom. H); 6.41 (*s*, H–C(5), minor isomer); 6.37 (*s*, H–C(5), major isomer); 2.32 (*s*, Me, minor isomer); 2.27 (*s*, Me, major isomer). ^{13}C-NMR ($CDCl_3$): 142.0, 137.7, 135.9, 132.9, 116.8 (5*s*, 5 arom. C, C(2), C(4)); 132.5, 132.0, 130.4, 130.2, 129.6, 128.5, 128.4, 128.2, 128.1, 128.0, 123.2, 121.0 (12*d*, 13 arom. CH); 96.9 (*d*, C(5)); 21.2 (*s*, Me, major isomer); 21.0 (*s*, Me, minor isomer). CI-MS: 473 (13), 472 (19), 471 (78), 470 (28), 469 (100, $[M+1]^+$), 468 (26), 467 (46), 466 (16), 465 (14). Anal. calc. for $C_{22}H_{17}BrN_2Se$ (468.25): C 56.43, H 3.66, N 5.98; found: C 56.33, H 3.64, N 6.00.

4.5. N-*(4-Chlorophenyl)-3-(4-methoxyphenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13e**). From 0.6 g (1.77 mmol) of **16e** and 0.35 g (1.76 mmol) of phenacyl bromide: 0.6 g (77.92%) of **13e**. M.p. 200.0–200.7° (CH_2Cl_2/MeOH). IR: 3097*w*, 3052*w*, 3013*w*, 2956*w*, 2930*w*, 2903*w*, 2833*w*, 1614*s*, 1603*s*, 1577*s*, 1556*m*, 1509*s*, 1481*s*, 1463*m*, 1451*m*, 1442*m*, 1346*m*, 1309*m*, 1300*m*, 1285*m*, 1247*s*, 1168*m*, 1146*s*, 1087*m*, 1067*m*, 1029*m*, 1008*m*, 919*w*, 872*m*, 832*s*, 821*m*. ^{1}H-NMR ($CDCl_3$): 7.26, 6.97 ($AA'BB'$, J_{AB} = 8.7, 4 arom. H); 7.19–7.10 (*m*, 7 arom. H); 6.79 (BB' of $AA'BB'$, J_{AB} = 8.9, 2 arom. H); 6.35 (*s*, H–C(5)); 3.73 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 158.8, 151.8, 142.0, 133.0, 131.4, 129.0 (6*s*, 5 arom. C, C(2), C(4)); 130.2, 130.0, 129.7, 128.7, 128.2, 128.1, 122.8, 114.3 (8*d*, 13 arom. C); 96.5 (*d*, C(5)); 55.3 (*q*, MeO). CI-MS: 445 (6), 444 (11), 443 (44), 442 (26), 441 (100, $[M+1]^+$), 440 (20), 439 (49), 438 (18), 437 (17). Anal. calc. for $C_{22}H_{17}ClN_2OSe$ (439.80): C 60.08, H 3.90, N 6.37; found: C 60.01, H 3.95, N 6.38.

4.6. N-*(4-Chlorophenyl)-3-(4-methylphenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13f**) *and 3-(4-Chlorophenyl)-*N*-(4-methylphenyl)-4-phenyl-1,3-selenazol-2(3*H*)-imine* (**13f'**). From 0.5 g (1.5 mmol) of **16f** and 0.3 g (1.5 mmol) of phenacyl bromide: 0.6 g (92.3%) of **13f**. M.p. 191.1–191.3° (CH_2Cl_2/MeOH). IR: 3108*w*, 3051*w*, 3033*w*, 2918*w*, 2855*w*, 1630*s*, 1620*s*, 1606*s*, 1580*s*, 1509*m*, 1481*s*, 1441*m*, 1350*m*, 1307*w*, 1293*m*, 1246*m*, 1165*w*, 1141*s*, 1105*w*, 1087*m*, 1066*m*, 1028*w*, 1009*m*, 916*m*, 869*m*, 831*m*, 821*m*. ^{1}H-NMR ($CDCl_3$, 2 isomers 4:1): 7.30–6.95 (*m*, 13 arom. H); 6.44 (*s*, H–C(5), minor isomer); 6.39 (*s*, H–C(5), major isomer); 2.32 (*s*, Me, minor isomer); 2.27 (*s*, Me, major isomer). ^{13}C-NMR ($CDCl_3$): 142.1, 142.0, 137.5, 132.8 (4*s*, 5 arom. C, C(2), C(4)); 130.3, 130.2, 129.7, 129.3, 128.7, 128.6, 128.3, 128.1, 123.0, 121.4 (10*d*, 13 arom. H); 97.3 (*d*, C(5)); 21.2 (*s*, Me, major isomer); 21.0 (*s*, Me, minor isomer). CI-MS: 429 (6), 428 (11), 427 (44), 426 (26), 425 (100, $[M+1]^+$), 424 (20), 423 (49), 422 (19), 421 (17). Anal. calc. for $C_{22}H_{17}ClN_2Se$ (423.80): C 62.35, H 4.04, N 6.61; found: C 62.19, H 4.13, N 6.60.

5. *X-Ray Structure-Determination of* **13a** *and* **13c** (*Table*, and *Figs. 1* and *2*)[2]). All measurements were performed on a *Nonius KappaCCD* diffractometer [31] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [32]. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections based on the multi-scan method [33] were applied. The structure of **13a** was solved by direct methods using SIR92 [34], which revealed the positions of all non-H-atoms. The structure of **13c** was solved by heavy-atom *Patterson* methods [35], which revealed the positions of the Br- and Se-atoms. All remaining non-H-atoms were located in a *Fourier* expansion of the *Patterson* soln., which was performed by *DIRDIF94* [36]. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom (1.5 U_{eq} for Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$). Corrections for secondary extinction were not applied. In the case of **13c**, several large peaks of residual electron density remain unaccounted for and cannot be associated with any logical chemical species. It is presumed that they are artefacts caused by the inferior data quality. Neutral atom scattering factors for non-H-atoms were taken from [37a], and the scattering factors for H-atoms were taken from [38]. Anomalous dispersion effects were included in F_c [39]; the values for f' and f'' were those of [37b]. The values of the mass-attenuation coefficients are those of [37c]. All calculations were performed using the SHELXL97 [40] program.

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[2]) CCDC-757788 and -757789 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table. *Crystallographic Data for Compounds* **13a** *and* **13c**

	13a	**13c**
Crystallized from	Et_2O	Et_2O
Empirical formula	$C_{21}H_{14}Br_2N_2Se$	$C_{23}H_{20}BrN_3Se$
Formula weight	533.06	497.24
Crystal color, habit	colorless, needle	colorless, needle
Crystal dimensions [mm]	$0.05 \times 0.05 \times 0.35$	$0.02 \times 0.05 \times 0.27$
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
Reflections for cell determination	45874	64681
2θ Range for cell determination [°]	4–50	4–55
Unit cell parameters a [Å]	5.7698(2)	5.9821(2)
b [Å]	23.1139(8)	10.9232(5)
c [Å]	14.3302(5)	15.9088(7)
α [°]	90	100.029(2)
β [°]	93.394(2)	97.181(3)
γ [°]	90	99.019(3)
V [Å^3]	1907.8(1)	998.53(7)
D_x [g cm^{-1}]	1.856	1.654
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	6.176	3.900
Scan type	ϕ and ω	ϕ and ω
$2\theta_{(\max)}$ [°]	50	55
Transmission factors (min; max)	0.522; 0.744	0.770; 0.928
Total reflections measured	31960	22568
Symmetry independent reflections	3356	4556
Reflections with $I > 2\sigma(I)$	2501	3474
Reflections used in refinement	3356	4556
Parameters refined	235	255
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0360	0.0812
$wR(F^2)$ (all data)	0.0769	0.2430
Weighting parameters [a; b][a])	0.0342; 1.1353	0.1645; 1.3205
Goodness of fit	1.042	1.089
Final $\Delta_{\max}/\sigma$	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.44; −0.47	3.62; −0.75

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

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