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SYNTHESIS OF 1,3,5-TRIAZINESELONES FROM IMIDOYL ISOSELENOCYANATES AND AMIDINES

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Dedicated to Prof. Dr. Albert Padwa on the occasion of his 75th birthday

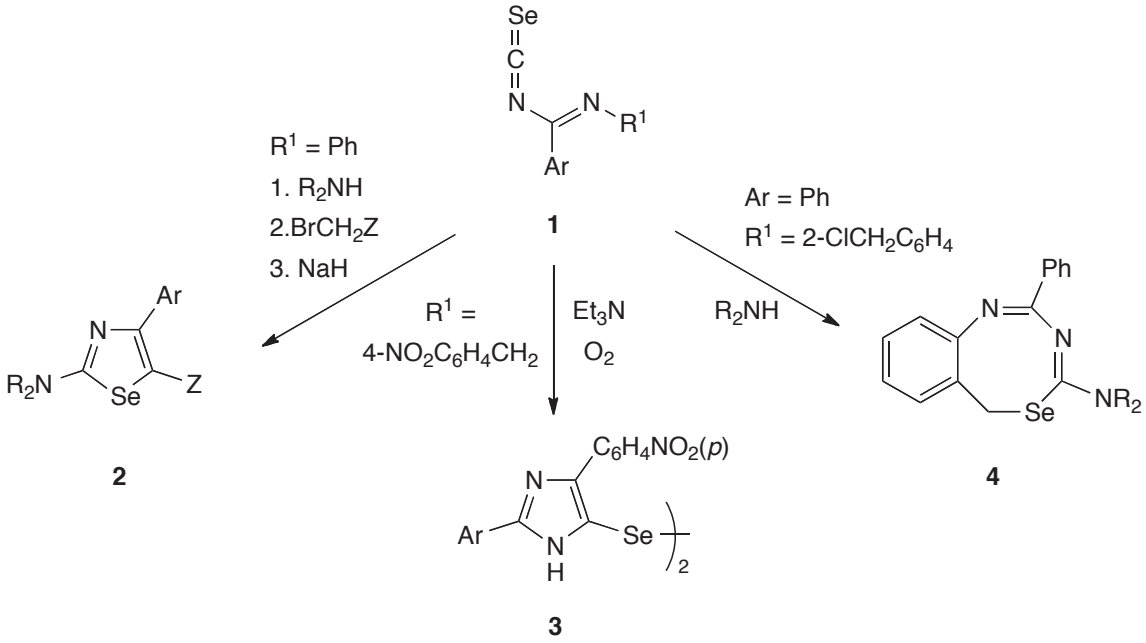
Abstract – Whereas the reaction of *N*-phenylbenzimidoyl isoselenocyanate (**1a**) with *N*-phenylbenzamidine (**5a**) at room temperature gave the corresponding 1,3,5-triazine-2(1*H*)-selone (**6a**), the analogous reaction with the unsubstituted benzamidine (**5b**) led to di-1,3,5-triazin-2-yl diselenide (**7b**) *via* oxidative dimerization of the intermediate 1,3,5-triazine-2-selenol. In a similar manner, **1** and 2-amino-3,4,5,6-tetrahydropyridine (**8**) yielded the cyclohexa-1,3,5-triazine-4-selone (**9**), which, in the presence of a strong base, reacted with a second molecule of isoselenocyanate to give the tricyclic 1,3,5-triazineselone (**10**). Finally, 2-amino-4,5-dihydro-1,3-thiazole (**11**) underwent the reaction with various isoselenocyanates (**1**) to yield 1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selones (**12**).

INTRODUCTION

The interest in organic selenium-containing compounds is still very pronounced as a result of their chemical properties and biological activities.[2] Since the discovery of the pharmacological activities of ebselen (2-phenyl-1,2-benzoisoselenazol-3(2*H*)-one),[3] the significance of this[4] and other selenaheterocycles[5] as well as that of heterocyclic selones[6] increased continually. For this reason, safe and efficient syntheses of selenium-containing heterocycles are very much in demand.

In the last decade, a large number of preparations of Se-heterocycles by using isoselenocyanates as safe, conveniently accessible, and powerful building blocks have been published.[7] Some time ago, we have described reactions with imidoyl isoselenocyanates (**1**), which were easily prepared from *N*-phenylimidoyl chlorides and potassium selenocyanate.[8,9] The reaction of *N*-phenylbenzimidoyl

isoselenocyanates (**1**, R^1 = Ph) with secondary amines led to selenourea derivatives, which by treatment with α-bromoesters, amides, and nitriles, respectively, and subsequently with a base gave 1,3-selenazoles (**2**) in high yields[9] (*Scheme 1*). On the other hand, the *N*-(4-nitrobenzyl)benzimidoyl isoselenocyanates (**1**, R^1 = 4-$NO_2C_6H_4CH_2$) under basic conditions cyclized to give 1*H*-imidazole-5-selenolates, which underwent an oxidative dimerization to give diimidazol-5-yl diselenides (**3**).[10] Furthermore, the reaction of **1** bearing a 2-(chloromethyl)phenyl residue R^1 with amines led to [5,1,3]benzoselenadiazocines (**4**).[11]



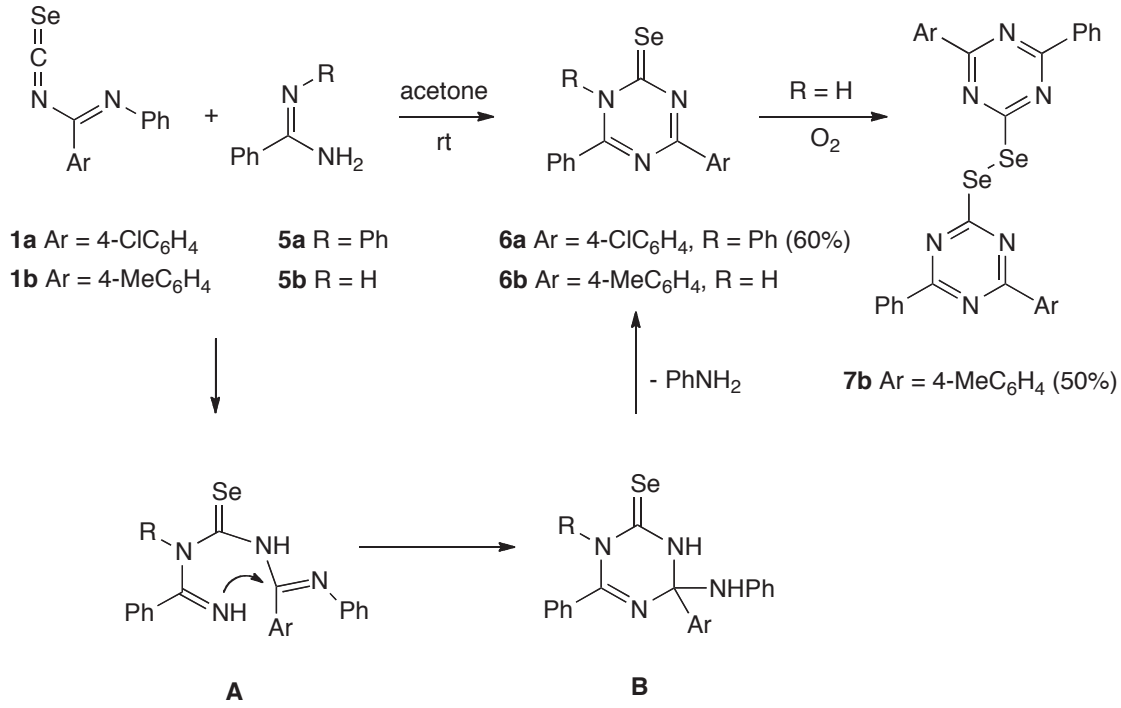
Scheme 1

The goal of the present study was the investigation of reactions of imidoyl isoselenocyanates (**1**, R^1 = Ph) with amidines as nucleophiles. Although many two- and three-component reactions of aryl isothiocyanates with amidines leading to five- and six-membered heterocycles are known,[12,13] there are, to the best of our knowledge, no analogous reactions with isoselenocyanates described.

RESULTS AND DISCUSSION

The starting materials, *i.e.* phenylbenzimidoyl isoselenocyanates (**1**), were conveniently prepared as described earlier[9] from *N*-phenylbenzamides by treatment with $SOCl_2$ and subsequent reaction of the formed imidoyl chloride with freshly prepared KSeCN. The reaction of **1a** (Ar = 4-ClC_6H_4) with *N*-phenylbenzamidine (**5a**) in acetone at room temperature for 1 h gave, after recrystallization from Et_2O/AcOEt, the crystalline product **6a** in 60% yield. On the basis of the NMR data as well as elemental analyses, the structure was determined as 1,3,5-triazine-2(1*H*)-selone (**6a**) (*Scheme 2*). Analogous

reactions with imidoyl isothiocyanates leading to the corresponding 1,3,5-triazine-2(1*H*)-thiones have been reported by Neuffer and Goerdeler.[14]



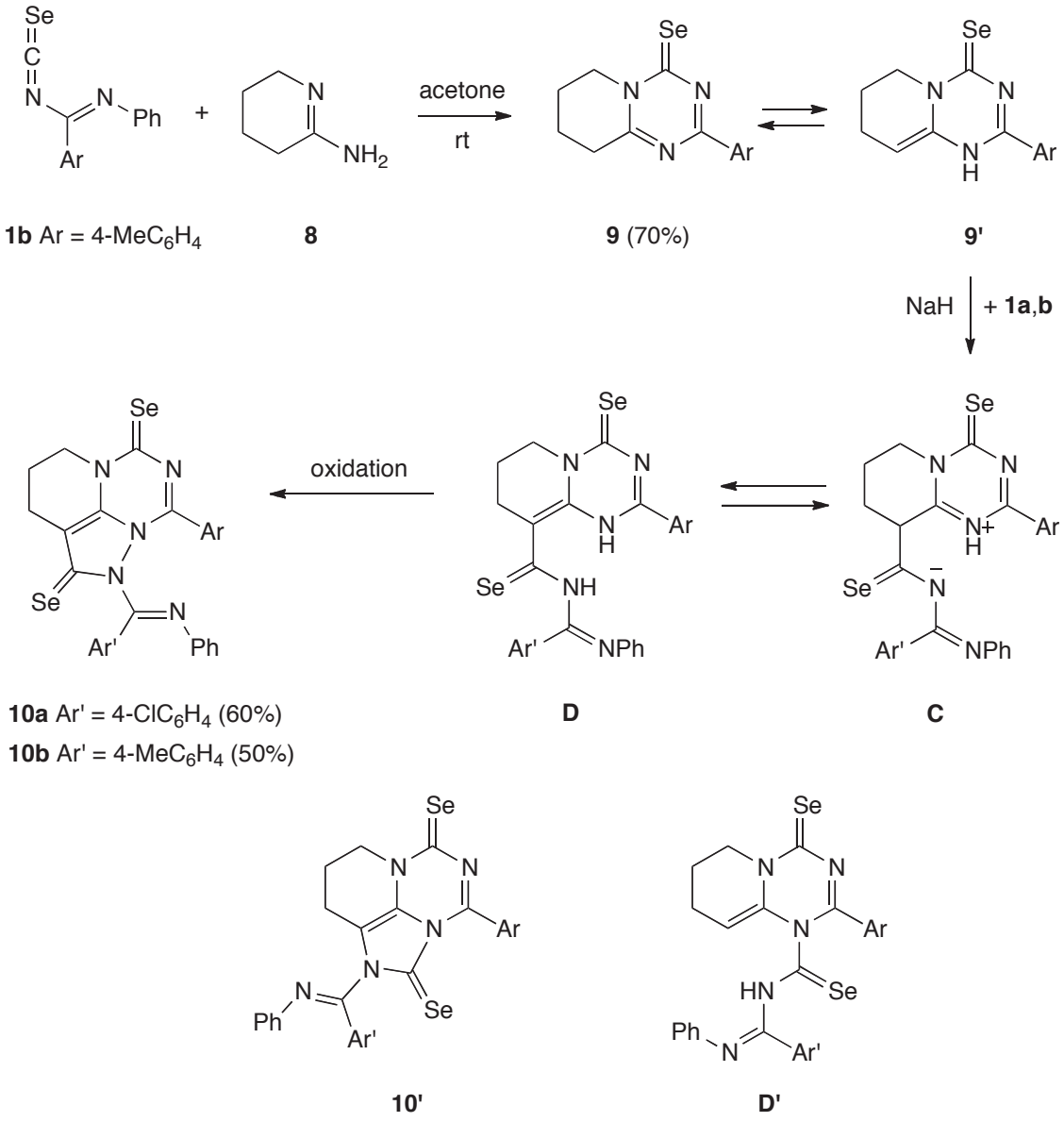
Scheme 2

The reaction of **1b** (Ar = 4-MeC_6H_4) with the unsubstituted benzamidine (**5b**, R = H) after 4 h under the same conditions gave the diselenide (**7b**), which is the product of the oxidative dimerization of the initially formed 1,3,5-triazine-2-selenol, the tautomer of **6b** (Ar = 4-MeC_6H_4, R = H). It is worth mentioning that corresponding triazine-2-thiones (R = H) could be isolated and are stable under similar conditions.[14]

A reaction mechanism for the formation of **6** is proposed in *Scheme 2*: the nucleophilic addition of the amidine (**5**) onto the heterocumulene C-atom of **1** leads to the selenourea intermediate (**A**), which undergoes the cyclization to give **B**. Spontaneous elimination of aniline yields the product of type **6**.

A similar reaction was observed between **1b** and 2-amino-3,4,5,6-tetrahydropyridine (**8**), which was generated *in situ* from the corresponding hydrochloride by treatment with potassium *tert*-butanolate, in acetone at room temperature. After 1 h, the expected bicyclic selone **9** was obtained in 70% yield (*Scheme 3*). This product may be transformed into the enamine (**9'**), which could undergo a second addition with an isoselenocyanate.[15] Therefore, a solution of **9** in dry THF was treated with 1.5 equiv. of NaH, and an equimolar amount of **1a** and **1b**, respectively, was added. After stirring for 1 h at room temperature, in each case one product was isolated, which, according to the NMR spectra contained the structure

elements of both reaction partners. For example, the products from the reaction with **1b** showed two sets of signals for 4-methylphenyl groups (*e.g.*, Me at 2.39/2.34 ppm and 21.5/21.4 ppm) and one for a phenyl group.

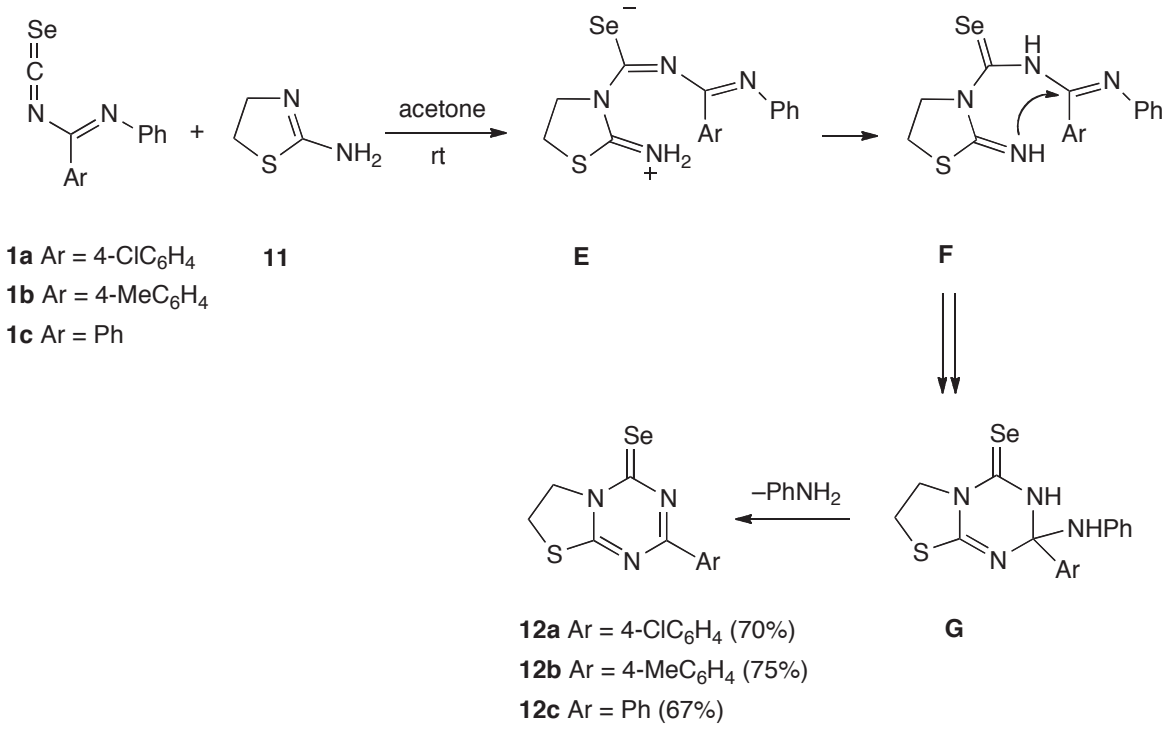


Scheme 3

First, we expected that compoud **D** or its isomer **D'** (*Scheme 3*) was formed. Surprisingly, ^{1}H-NMR and mass spectra as well as elemental analyses indicated the absence of two H-atoms. All data were in accordance with the structure of either **10** or **10'**, *i.e.* an oxidized product. Extensive NMR studies proved **10a** to be the correct structure. For example, the ^{1}H,^{13}C-HMBC data clearly indicated the three bond correlation of C=Se (170.3 ppm) in the five-membered ring[16] with the CH_2 group at 3.07 ppm of the

tetrahydropyridine ring. The formation of **10a**,**b** in the presence of NaH may be rationalized by C,C-bond formation between the anion of **9/9'** and **1** to give **C/D**, which, unexpectedly, undergoes an oxidative ring closure in the presence of O_2, either under the reaction conditions or during workup, to give the final product.

The third selected substrate with an amidine-like moiety was 2-amino-4,5-dihydro-1,3-thiazole (**11**). Its reaction with isoselenocyanates (**1a**–**c**) in acetone at room temperature proceeded smoothly and gave the fused 1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selone (**12**) in good yields of 67 – 75% (*Scheme 4*).[17] The structures of the products were deduced from their spectroscopic data and elemental analyses. Furthermore, analogous products have been obtained earlier from the reaction of imidoyl isothiocyanates with 2-amino-1,3-thiazole.[18]



Scheme 4

Finally, the structure of **12a** was established by X-ray crystallography (*Figure 1*). The five-membered ring has an envelope conformation with C(8) as the envelope flap. Apart from this atom, the whole molecule is essentially planar. The plane of the chlorophenyl substitutent and the mean plane of the fused six-membered ring have a dihedral angle of only 5.0(1)°. This latter ring is however slightly puckered into a butterfly conformation folded along the C(1)···N(4) axis, where the planes of the two sides of the ring intersect at an angle of 4.7(2)°. This folding causes N(2) and C(7) to deviate slightly from the overall mean plane of the molecule.

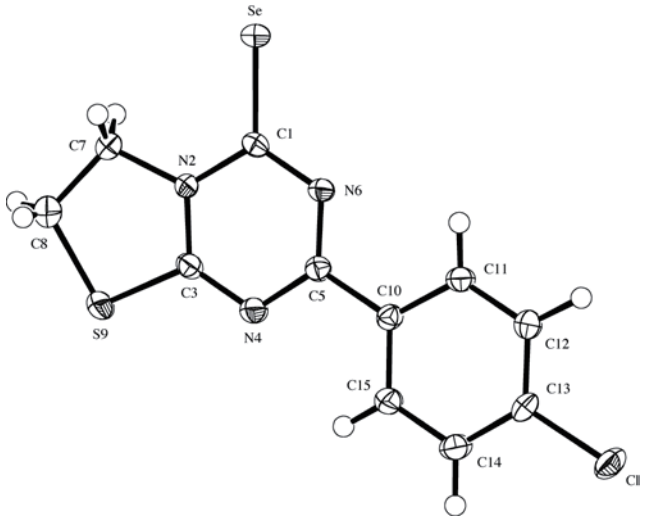


Figure 1. ORTEP plot[19] of the molecular structure of **12a** (arbitrary numbering of the atoms; 50% probability ellipsoids)

Our mechanistic proposal for the formation of compounds (**12**) is analogous to that described above for the 1,3,5-triazine-2-selones (**6**) and (**9**): the nucleophilic addition of the ring N-atom of **11** at the electrophilic C-atom of **1** leads to the selenourea derivatives (**F**), which cyclize spontaneously to give **G**. Elimination of aniline then yields the product **12** (*Scheme 4*).

A similar reaction has been observed between **11** and carbethoxy isothiocyanate yielding 2,3,6,7-tetrahydro-4-thioxo-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazin-2-one as the only product.[20] This reaction was also extended to analogs of **11**, such as the corresponding 1,3-selenazole and 2-amino-5,6-dihydro-4*H*-1,3-thiazine.[20] On the other hand, **11** and benzoyl isothiocyanate in acetonitrile reacted to give three products, 6,7-dihydro-2-phenyl-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-thione, 1-benzoyl-3-(4,5-dihydro-1,3-thiazol-2-yl)thiourea, and 2-benzamido-4,5-dihydro-1,3-thiazolium thiocyanate.[21] These results were explained by a non-regioselective reaction of **11** with benzoyl isothiocyanate either *via* the ring N-atom or the exocyclic NH_2 group.

CONCLUSIONS

The present study shows that *N*-phenylimidoyl isoselenocyanates (**1**) react smoothly with amidines as nucleophiles in analogy to the corresponding imidoyl isothiocyanates.[14] In all investigated reactions, 1,3,5-triazine-2(1*H*)-selones are formed as the major products *via* a formal (3+3)-cycloaddition.[14] In the case of the N(1)-unsubstituted triazineselone (**6b**), a spontaneous oxidative dimerization yields the diselenide (**7b**), proving the generally observed higher tendency for oxidation processes of selenium compounds in comparison with analogous sulfur derivatives. The elaborated procedure offers a convenient access to 1,3,5-triazone-2(1*H*)-selones.

EXPERIMENTAL

General remarks. Thin layer chromatography (TLC) on silica gel 60 F_{254} plates (0.25 mm, Merck); hexane/AcOEt 1:1 or 2:1 as eluents. Column chromatography (CC) on silica gel 60 (0.040–0.063 mm; Merck). Melting points (mp): Büchi B-540 apparatus; in capillary, uncorrected. IR spectra: Perkin-Elmer-Spektrum 1600 FT-IR spectrophotometer; in KBr, in cm^{-1}. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 or 150 MHz) spectra: Bruker ARX-300 or AMX-600 instrument, in $CDCl_3$; chemical shifts in ppm, coupling constants *J* in Hz. The multiplicities of ^{13}C signals were determined with DEPT spectra. EI-MS (70 eV) and CI-MS (NH_3 as carrier gas): Finnigan MAT-95 or Finnigan SSQ-700 instrument. ESI-MS: Finnigan TSQ-700. Elemental analyses were carried out on a Gerber Elementar Analysator EL instrument.

Reactions of benzimidoyl isoselenocyanates (1) with benzamidines (**5**). To a stirred solution of **1**[9] (3.15 and 3.88 mmol, respectively) in acetone (20 – 50 mL) at rt was added the equimolar amount of **5a** and **5b**, respectively, and the mixture was stirred for 1 and 4 h, respectively. In the case of **5a**, the mixture was poured into ice-water and stirred for another 1 h. The formed precipitate was filtered and recrystallized from Et_2O/AcOEt to give 0.8 g (60%) of **6a**. In the case of **5b**, the formed precipitate in the mixture was filtered by suction and recrystallized from DMF yielding 0.64 g (50%) of **7b**.

4-(4-Chlorophenyl)-1,6-diphenyl-1,3,5-triazine-2(1*H*)-selone (**6a**). Colorless crystals. Mp 201 – 202 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.55, 7.47 (*AA'BB'*, J_{AB} = 8.7, 4 arom. H); 7.45 – 7.20 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.9 (*s*, C=Se); 167.4, 155.3 (2*s*, C(4), C(6)); 139.8, 136.8, 133.3, 132.7 (4*s*, 4 arom. C); 131.3, 131.2, 129.5, 129.3, 129.0, 128.7, 128.2, 128.1 (8*d*, 14 arom. CH). Anal. Calcd for $C_{21}H_{14}ClN_3Se$ (422.78): C, 59.66; H, 3.34; Cl, 8.39; N, 9.94. Found: C, 59.38; H, 3.55; Cl, 8.28; N 10.16.

Bis[4-(4-methylphenyl)-6-phenyl-1,3,5-triazine-2-yl] diselenide (**7b**). Colorless crystals. Mp 280 °C (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.58, 8.48 (*AA'BB'*, J_{AB} = 8.3, 4 arom. H); 7.54 – 7.43 (*m*, 3 arom. H); 7.28 – 7.25 (*m*, 2 arom. H); 2.42 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.0, 163.8 (2*s*, C(2), C(4), C(6)); 143.8, 140.8, 135.0 (3*s*, 3 arom. C); 135.0, 132.5, 129.3, 129.1, 128.5 (5*d*, 9 arom. CH); 21.8 (*q*, Me). CI-MS (NH_3): 655 (3), 654 (3), 653 (8, $[M+1]^+$), 652 (3), 651 (8), 650 (3), 649 (4), 573 (10), 330 (18), 329 (18), 328 (100), 327 (10), 326 (50), 325 (18), 324 (17). Anal. Calcd for $C_{32}H_{24}N_6Se_2$ (650.50): C, 59.08; H, 3.72; N, 12.92. Found: C, 59.45; H, 3.61; N 12.54.

Reaction of 1b with 2-amino-3,4,5,6-tetrahydropyridine (**8**). A mixture of **8** (490 mg, 5 mmol) and potassium *tert*-butanolate (*t*-BuOK, 560 mg, 5 mmol) in acetone (10 mL) was vigorously stirred for 20 min. Then, this suspension was added to a solution of 4-methyl-*N*-phenylbenzimidoyl isoselenocyanate (**1b**, 1.5 g, 5 mmol) in acetone (40 mL) at rt and the mixture was stirred for 1 h. After this time, no

starting material could be detected (TLC), and the red mixture was poured into ice-water and stirred for another 1 h. The formed precipitate was filtered by suction and dried in vacuum. Recrystallization from acetone/ethanol 1:1 yielded 1.06 g (70%) of **2-(4-Methylphenyl)cyclohexa-1,3,5-triazine-4-selone** (**9**) as colorless crystals. Mp 198.5 – 200 °C. IR (KBr): 2957*w*, 2921*w*, 2866*w*, 1608*w*, 1578*m*, 1538*s*, 1512*s*, 1486*s*, 1438*m*, 1405*s*, 1392*s*, 1335*m*, 1313*m*, 1285*m*, 1273*m*, 1249*m*, 1172*m,* 1155*m*, 1111*m*, 1059*m*, 965*m*, 868*m*, 836*m*, 822*m*, 769*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.39, 7.26 (*AA'BB'*, J_{AB} = 8.0, 4 arom. H); 4.37 (*t*, *J* = 6.3, CH_2); 3.04 (*t*, *J* = 6.5, CH_2); 2.40 (*s*, Me); 2.15 – 2.02, 2.00 – 1.90 (2*m*, 2 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 188.5 (*s*, C=Se); 167.4, 161.8 (2*s*, C(2), C(9a)); 144.3, 130.9 (2*s*, 2 arom. C); 130.1, 129.3 (2*d*, 4 arom. CH); 53.8, 32.3, 22.6, 18.4 (4*t*, 4 CH_2); 21.7 (*q*, Me). CI-MS (NH_3): 308 (20), 307 (14), 306 (100, $[M+1]^+$), 305 (8), 304 (49), 303 (16), 302 (17), 258 (12), 226 (14), 208 (29). Anal. Calcd for $C_{14}H_{15}N_3Se$ (304.25): C, 55.27; H, 4.97; N, 13.81. Found: C, 55.28; H, 4.95; N 13.56.

Reaction of 1 with 9. A mixture of **9** (304 mg, 1.0 mmol and 152 mg, 0.5 mmol, resp.) and NaH (36 mg, 1.5 mmol) in dry THF (20 mL) was stirred at rt until a clear solution was formed. Then, **1a** or **1b** (320 mg and 300 mg, resp., 1.0 mmol) was added, the deep orange mixture was stirred for 1 h, and was poured into ice-water while stirring. After addition of some $MgSO_4$, the mixture was stirred for another 1 h, the precipitate was filtered by suction and recrystallized from AcOEt yielding the tricyclic bis-selone **10**.

2-(4-Chloro-*N*-phenylbenzimidoyl)-3-(4-methylphenyl)-2a,5,5a,6,7,8-hexahydro-2,2a,4,5-tetraaza-acenaphthene-1,5-diselone (10a): 0.364 g (60%). Pale yellow crystals. Mp 267 °C (dec.). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13 (*AA'* of AA'BB', J_{AB} = 8.2, 2 arom. H); 7.51 (*AA'* of AA'BB', J_{AB} = 8.6, 2 arom. H); 7.38 – 7.23 (*m*, 7 arom. H); 7.08 – 7.05 (*m*, 2 arom. H); 4.55 (*t*, *J* = 5.9, CH_2); 3.07 (*t*, *J* = 6.1, CH_2); 2.39 (*s*, Me); 2.17 (*quint*, *J* ≈ 6, CH_2). ^{13}C-NMR (150 MHz, $CDCl_3$): 187.1, 170.3 (2*s*, 2 C=Se); 163.5, 158.8, 153.5, 143.0, 139.0, 137.2, 131.8, 129.5, 100.8 (9*s*, 2 C=N, 5 arom. C, C=$C(N)_2$); 131.3, 129.9, 129.7, 129.2, 128.6, 127.6, 125.6 (7*d*, 13 arom. CH); 53.3, 22.4, 20.5 (3*t*, 3 CH_2); 21.6 (*q*, Me). CI-MS (NH_3): 626 (20), 625 (11), 624 (42, $[M+1]^+$), 623 (13), 622 (34), 621 (13), 620 (16), 562 (17), 561 (44), 560 (44), 559 (92), 558 (24), 557 (48), 556 (16), 555 (14), 333 (25), 332 (21), 331 (100), 329 (46), 328 (16), 327 (16). Anal. Calcd for $C_{28}H_{22}ClN_5Se_2$ (621.89): C, 54.08; H, 3.57; N, 11.26; Cl, 5.70. Found: C, 54.36; H, 3.58; N 10.91; Cl, 5.69.

2-(4-Methyl-*N*-phenylbenzimidoyl)-3-(4-methylphenyl)-2a,5,5a,6,7,8-hexahydro-2,2a,4,5-tetraaza-acenaphthene-1,5-diselone (10b): 0.11 g (50%). Pale yellow crystals. Mp 256 – 257 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15 (*AA'* of AA'BB', J_{AB} = 8.2, 2 arom. H); 7.45 (*AA'* of AA'BB', J_{AB} = 8.2, 2 arom. H); 7.40 – 7.23 (*m*, 5 arom. H); 7.15 – 7.05 (*m*, 4 arom. H); 4.56 (*t*, *J* = 5.9, CH_2); 3.08 (*t*, *J* = 6.1, CH_2); 2.39, 2.34 (2*s*, 2 Me); 2.16 (*quint*, *J* ≈ 6, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 187.1, 170.6 (2*s*, 2 C=Se); 164.8,

158.9, 153.4, 142.8, 141.5, 139.3, 132.0, 128.1, 100.4 (9*s*, 2 C=N, 5 arom. C, C=$C(N)_2$); 130.3, 129.9, 129.6, 129.1, 129.0, 127.4, 125.6 (7*d*, 13 arom. CH); 53.3, 22.4, 20.5 (3*t*, 3 CH_2); 21.5, 21.4 (2*q*, 2 Me). CI-MS (NH_3): 606 (11), 605 (11), 604 (36, $[M+1]^+$), 603 (12), 602 (32), 601 (14), 600 (17), 333 (16), 332 (14), 331 (85), 330 (7), 329 (41), 328 (15), 327 (15), 276 (56), 251 (100). Anal. Calcd for $C_{29}H_{25}N_5Se_2$ (601.47): C, 57.91; H, 4.19; N, 11.64. Found: C, 57.69; H, 4.14; N 11.67.

Reactions of 1 with 2-amino-4,5-dihydro-1,3-thiazole (**11**). To a stirred solution of **1** (3 – 4.5 mmol) in acetone (20 mL) at rt was added the equivalent amount of **11**. Immediately, a yellow to orange precipitate formed. After stirring the mixture for 1 h, the formed precipitate was filtered by suction, washed with some acetone, and dried in vacuum. The products were recrystallized from acetone or DMF.

2-(4-Chlorophenyl)-6,7-dihydro-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selone (**12a**). Yield: 0.73 g (70%); from 990 mg (3.1 mmol) **1a**, 316 mg (3.1 mmol) **11**. Orange crystals. Mp 283.5 – 284.5 °C (acetone/DMF). IR (KBr): 3073*w*, 2997*w*, 2951*w*, 1590*w*, 1576*m*, 1531*s*, 1491*m*, 1435*s*, 1396*s*, 1380*s*, 1347*m*, 1313*m*, 1295*m*, 1266*s*, 1224*m*, 1199*m,* 1179*m*, 1166*m*, 1136*m*, 1101*m*, 1085*m*, 1063*m*, 1008*m*, 843*m*, 825*m*, 771*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.43, 7.44 (*AA'BB'*, J_{AB} = 8.8, 4 arom. H); 4.89 (*t*, *J* = 8.1, CH_2); 3.50 (*t*, *J* = 8.1, CH_2). ^{13}C-NMR (150 MHz, $CDCl_3$): 185.1 (*s*, C=Se); 170.9, 167.4 (2*s*, C(2), C(8a)); 139.5, 132.3 (2*s*, 2 arom. C); 131.1, 128.7 (2*d*, 4 arom. CH); 57.1, 23.1 (2*t*, 2 CH_2). EI-MS: 331 (7), 329 (16, $[M+1]^+$), 327 (8), 223 (9), 217 (10), 162 (13), 138 (15), 137 (21), 111 (23), 102 (21), 86 (26), 85 (100). Anal. Calcd for $C_{11}H_8ClN_3SSe$ (328.68): C, 40.20; H, 2.45; N, 12.78; S, 9.76. Found: C, 40.19; H, 2.44; N 12.76; S, 9.67.

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

6,7-Dihydro-2-(4-methylphenyl)-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selone (**12b**). Yield: 0.72 g (75%); from 930 mg (3.1 mmol) **1b**, 316 mg (3.1 mmol) **11**. Orange crystals. Mp 270 °C (dec., DMF). IR (KBr): 2948*w*, 1608*w*, 1574*w*, 1530*s*, 1509*m*, 1430*s*, 1402*m*, 1380*s*, 1348*m*, 1305*m*, 1267*s*, 1223*m*, 1171*m*, 1137*m*, 1061*w*, 1014*w*, 988*w*, 834*m*, 768*m*. CI-MS (NH_3): 312 (21), 311 (14), 310 (100, $[M+1]^+$), 309 (8), 223 (7), 308 (51), 307 (17), 306 (16), 246 (22). Anal. Calcd for $C_{12}H_{11}N_3SSe$ (308.27): C, 46.76; H, 3.60; N, 13.63; S, 10.40. Found: C, 46.66; H, 3.56; N 13.58; S, 10.37.

6,7-Dihydro-2-phenyl-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selone (**12c**). Yield: 0.68 g (67%); from 970 mg (3.4 mmol) **1c**, 347 mg (3.4 mmol) **11**. Orange crystals. Mp 235.5 – 236.1 °C (acetone/DMF). IR (KBr): 3034*w*, 2970*w*, 1581*w*, 1538*s*, 1494*w*, 1461*s*, 1445*m*, 1421*s*, 1384*s*, 1357*m*, 1309*m*, 1292*m*, 1270*s*, 1247*m*, 1228*m*, 1201*m,* 1171*m*, 1139*m*, 1069*m*, 849*m*, 825*m*, 743*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.51 – 8.45 (*m*, 2 arom. H); 7.63 – 7.57 (*m*, 1 arom. H); 7.49 – 7.26 (*m*, 2 arom. H); 4.89 (*t*, *J* = 8.1, CH_2); 3.50 (*t*, *J* = 8.1, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 184.4 (*s*, C=Se); 173.8, 163.2 (2*s*, C(2), C(8a)); 133.4 (*s*, 1

arom. C); 133.8, 130.6, 128.7 (3*d*, 5 arom. CH); 57.4, 23.1 (2*t*, 2 CH_2). CI-MS (NH_3): 298 (20), 297 (12), 296 (100, $[M+1]^+$), 295 (7), 294 (48), 293 (16), 292 (16), 261 (7),256 (29), 248 (25), 232 (13), 231 (20). Anal. Calcd for $C_{11}H_9N_3SSe$ (294.24): C, 44.90; H, 3.08; N, 14.28; S, 10.90. Found: C, 44.98; H, 3.02; N 14.29; S, 11.06.

X-Ray Crystal-Structure Determination of **12a** (*Figure 1*).[22] All measurements were made on a Rigaku AFC5R diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) and a 12kW rotating anode generator. Data collection and refinement parameters are given below, and a view of the molecule is shown in *Figure 1*. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans of several relfections[23] was applied. Equivalent reflections were merged. The structure was solved by direct methods using SIR92,[24] which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were located in a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. Refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2-F_c^2)^2$. A correction for secondary extinction was applied. Neutral atom scattering factors for non-H-atoms were taken from ref.[25], and the scattering factors for H-atoms were taken from ref.[26] Anomalous dispersion effects were included in F_C;[27] the values for f' and f'' were those of ref.[28] The values of the mass attenuation coefficients are those of ref.[29] All calculations were performed using the SHELX97 program.[30] Crystal data for **12a**: Crystallized from acetone/DMF, $C_{11}H_8ClN_3SSe$, M = 328.62, red, prism, crystal dimensions 0.22 × 0.33 × 0.48 mm, triclinic, space group $P\bar{1}$, Z = 2, reflections for cell determination 25, 2θ range for cell determination 39–40°, a = 7.304(2) Å, b = 8.074(3) Å, c = 11.198(2) Å, α = 75.41(2), β = 74.39(2)°, γ = 71.83(2), V = 593.9(3) Å^3, D_X = 1.837 g·cm^{-3}, μ(MoK_α) = 3.537 mm^{-1}, T = 173(1) K, $\omega/2\theta$ scans, $2\theta_{max}$ = 55°, transmission factors (min; max) 0.706; 1.000, total reflections measured 2934, symmetry independent reflections 2742, reflections with $I > 2\sigma(I)$ 2319, reflections used in refinement 2742, parameters refined 154, final R ($I > 2\sigma(I)$ reflections) = 0.0278, wR (all data)= 0.0684 ($w = [\sigma^2(F_o^2) + (0.0328P)^2 + 0.2897P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$, goodness of fit 1.043, final Δ_{max}/σ = 0.001, $\Delta\rho$ (max; min) = 0.42; –0.36 e Å^{-3}.

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