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SYNTHESIS AND REACTIONS OF 1,3,4-SELENADIAZINES

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Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday

Abstract – Various 1,3,4-selenadiazines were prepared by cyclization of selenosemicarbazides with phenacyl bromides. The compounds generally exist in their 6*H*-tautomeric form and contain an exocyclic imino group in the solid state. 1,3,4-4*H*-Selenadiazines, available from 1,2-dimethylated selenosemicarbazides, cannot be isolated because they rapidly undergo a deselenation reaction under the conditions of their formation. Deselenation can be induced for 1,3,4-6*H*-selenadiazines under forcing conditions by reflux of a solution in glacial acetic acid. On the other hand, a ring contraction is observed when concentrated HCl or HBr is used.

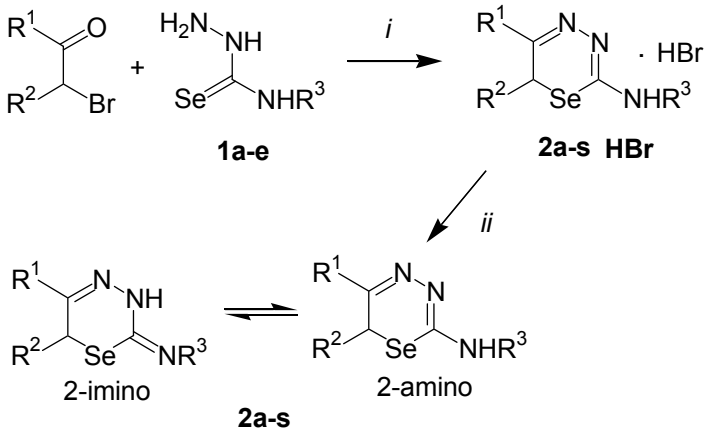
INTRODUCTION

Selenium represents an essential element for higher organisms and selenium containing enzymes, such as *Glutathioneperoxidase* and *5'-Deiodase type 1,* play an important role in the organism.[1] Selenium containing molecules, such as the antitumor and antiviral C-glycosyl selenazole selenazofurin, are of considerable pharmacological importance because selenium deficiency can result in a number of diseases.[2-4] However, selenium heterocycles are mostly less stable as compared to their sulfur analogues. In

addition, the methods and conditions available for the synthesis of sulfur compounds can often not be applied to selenium. Therefore, the development of new methods for the synthesis of small selenium-containing building blocks is of considerable current interest. In this context, 1,3,4-selenadiazines represent an interesting type of heterocycle because they can easily deliver selenium by ring contraction. In contrast to 1,3,4-thiadiazines, 1,3,4-selenadiazines and isomeric selenadiazines have only scarcely been reported in the literature.[5] Some years ago, Zimmermann and coworkers reported studies related to the pharmacological properties of 1,3,4-thiadiazines and 1,3,4-selenadiazines, such as cardiotonic activity.[5g,h] Their synthesis of 1,3,4-selenadiazines was reported by Bulka and coworkers in 1963 at the University of Greifswald.[6] Some of us earlier reported, based on the initial work of Bulka,[6] the synthesis of a number of 2-imino-2,3-dihydro-6*H*-1,3,4-selenadiazines by cyclization of selenosemicarbazides with phenacyl bromides and also studied chemical reactions, such as the deselenation, of these products.[8-10] This work was mainly published in the form of short articles without providing a complete experimental section and comprehensive compound characterization. Since our early reports, we systematically explored the preparative scope and completely characterized new compounds in solution and in the solid state by modern sprectroscopic techniques. Herein, we wish to report a comprehensive study of the synthesis, reactions and structural characterization of a great variety of 1,3,4-selenadiazines. With regard to our earlier reports, the scope was extended and all new compounds were characterized by modern spectroscopic methods (although in some cases NMR spectra could not be obtained due to solubility problems). To get some deeper insight to structural parameters, we also studied the solid state structure of a number of 1,3,4-selenadiazines by X-ray crystal structure analyses.[11] In fact, only very few X-ray crystal structure analyses of 1,3,4-selenadiazines have been previously reported in the literature.[9]

RESULTS AND DISCUSSION

Cyclizations of 1,2-unsubstituted selenosemicarbazides. Reflux of an ethanol solution of 1,2-unsubstituted selenosemicarbazides **1a-e** with various phenacyl bromides afforded the 1,3,4-6*H*-selenadiazines **2a-s** in the form of their hydrobromides in good yields (Scheme 1, Table 1). The hydrobromides were transformed into the corresponding free bases by treatment with an aqueous solution of ammonia. In case of **2b,c,r,s** ammonia was directly added to the reaction mixture when the cyclization was complete and the free base was isolated without prior isolation of the hydrobromide. It is worthy to note that parent selenosemicarbazide could be successfully employed and afforded product **2s** in excellent yield. In case of **2o**, **2k**, **2p**, and **2l**, the 2-iminoselenazoles **3a**, **3b**, **3c**, and **3d** were formed as by-products by a ring contraction reaction, respectively (*vide infra*). In addition, traces of 2-hydrazinoselenazoles were formed (Scheme 2, Table 2).

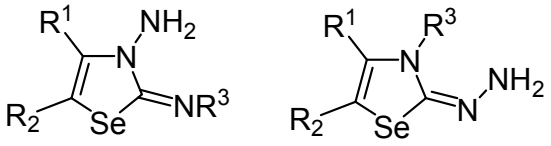


Scheme 1. Synthesis of 1,3,4-selenadiazines **2a-s**: *conditions*: *i*, reflux, EtOH or *i*PrOH, 48% HBr; *ii*, aq. ammonia

Table 1. Synthesis of 1,3,4-selenadiazines **2a-s**

2	**3**	R^1	R^2	R^3	% (**2**·HBr) [a]	% (**2**) [b]	% (**3**) [c]
a		Ph	Ph	Ph	74	100	-
b		Ph	Me	Ph	-	61	-
c		Ph	H	Ph	-	72	-
d		BrC_6H_4	H	Ph	86	100	-
e		ClC_6H_4	H	Ph	56	100	-
f		MeC_6H_4	H	Ph	74	100	-
g		Ph	Ph	*t*Bu	85	100	-
h		Ph	Me	*t*Bu	80	82	-
i		Ph	H	*t*Bu	96	100	-
j		ClC_6H_4	H	*t*Bu	76	100	-
k	**b**	Ph	Ph	*i*Pr	61	100	34
l	**d**	Ph	Me	*i*Pr	78	100	17
m		Ph	H	*i*Pr	96	100	-
n		ClC_6H_4	H	*i*Pr	76	100	-
o	**a**	Ph	Ph	Pr	70	100	14
p	**c**	Ph	Me	Pr	82	100	7
q		Ph	H	Pr	89	100	-
r		ClC_6H_4	H	Pr	-	85	-
s		ClC_6H_4	H	H	-	100	-

[a] Yield of isolated hydrobromide. [b] Yield of isolated free base (based on **2**·HBr); for **2b,c,r,s** yield of isolated free base (based on **1**). [c] Yield of isolated by-products **3** (structures are given below)



Bilinski *et al.* reported the synthesis of 1,3,4-selenadiazines by ring-expansion reactions of selenazolines.[7] While most 1,3,4-selenadiazines exist in their 6*H* tautomeric form, Bobylew reported 1,3,4-selenadiazines existing in their 4*H* form.[12] The structure of 1,3,4-6*H*-selenadiazines **2a-s** was established by spectroscopic methods. The NMR data clearly show that all 1,3,4-selenadiazines reside in their 6*H*-form containing a sp^3 hybridized carbon atom *C*HR.[2] This can be explained by the fact that the 4*H*-isomer would have an unstable 8π system. However, it is unclear whether the compounds reside in their 2-imino or 2-amino tautomeric form. Only one set of signals is observed. This might be due to the fact that the equilibrium is fast on the NMR time scale or by the fact that only one tautomer is present. The structure of **2m** was independently confirmed by X-ray crystal structure analysis (Figure 1).[11] The location of the H-atom located at N1 was determined by the difference electron density and refined freely. According to this calculation, the compound resides, in the solid state, in the 2-imino tautomeric form. Of course, the structure in the solid state does not allow to draw a conclusion regarding the structure in solution. Therefore, the solution structure (imino *versus* amino tautomer) remains unclear at present. For derivative **2s** (R^3 = H), only one signal was observed for the NH protons in the ^{1}H NMR spectrum which suggests that the molecule exists in the amino tautomeric form. However, a rapid equilibrium between two different NH protons cannot be excluded.

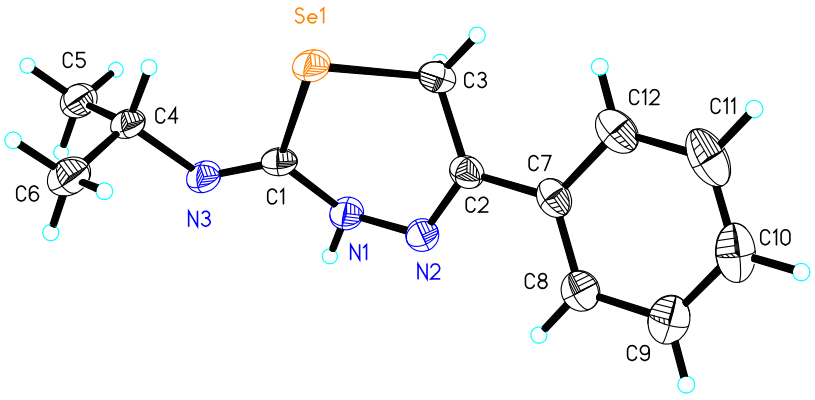
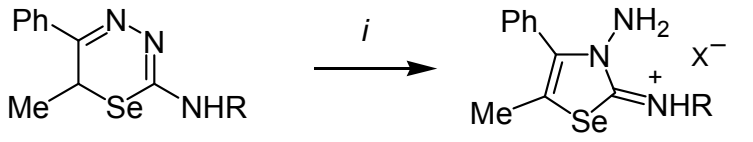


Figure 1. ORTEP-Plot of **2m** (50% probability level, the location of the H-atom located at N1 was determined by the difference electron density and refined freely)

It was mentioned above, that derivatives **3a-d** were obtained in low yields as side-products during the formation of 1,3,4-6*H*-selenadiazines **2**. To further study this reaction, 1,3,4-6*H*-selenadiazines **2l** and **2p** were treated with a concentrated solution of hydrochloric acid (37%) or hydrobromic acid (48%). These reactions resulted in ring contraction to give the 2-iminoselenazoles **3c** and **3d** in high yields, respectively (Scheme 2, Table 2). The ring contraction can be explained in analogy to the mechanism suggested by Busby *et al.*[13] for the analogous ring contraction of 1,3,4-6*H*-thiadiazines which represent sulphur analogues of products **2**.



2l,p **3c,d** (X = Cl, Br)

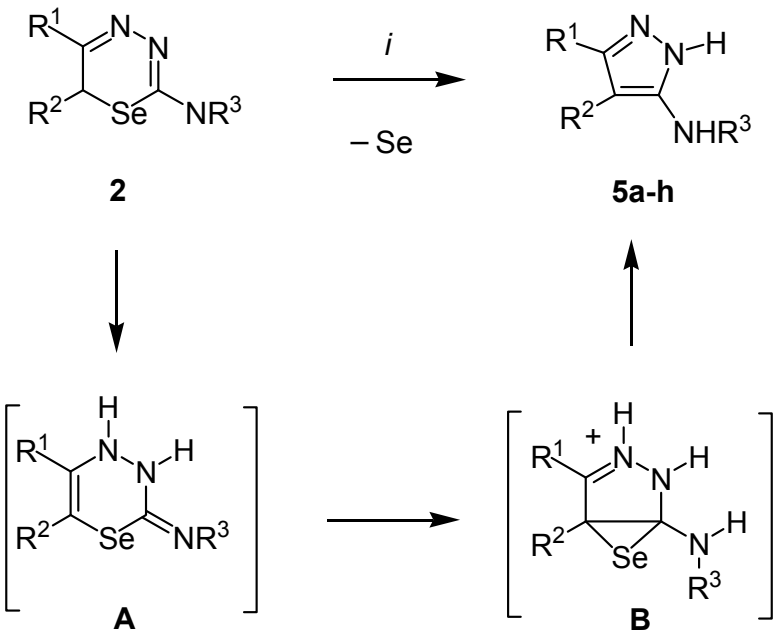
Scheme 2. Ring contraction of 1,3,4-selenadiazines **2l,p**: *conditions*: HCl (37% aq. solution) or HBr (48% aq. solution)

Table 2. Ring contraction of 1,3,4-selenadiazines **2l,p**

3	R	**3·HCl** (%)[a]	**3·HBr** (%)[a]
c	*n*Pr	60	87
d	*i*Pr	67	92

[a] Isolated yields

It is interesting to note that reflux of a solution of 1,3,4-6*H*-selenadiazines **2** in glacial acetic acid resulted in extrusion of selenium and formation of pyrazoles **5a-h** instead of ring contraction (Scheme 3, Table 3). The formation of the products can be explained by formation of 1,3,4-4*H*-selenadiazine intermediate **A**, valence isomerization into the selena-σ-homopyrazole **B**, and subsequent extrusion of selenium. The deselenation can be explained in analogy to the desulfurization of 1,3,4-6*H*-thiadiazines which was previously studied in detail.[14] It is worthy to note that the deselenation can be also carried out using trifluoroacetic acid and trifluoroacetic anhydride[8c] or triphenyl phosphane.[16] The product distribution (deselenation or ring contraction) depends on the type of substituent R^1, R^2, R^3 and on the type of acid employed which might be explained by the extent of protonation during the course of the reaction.



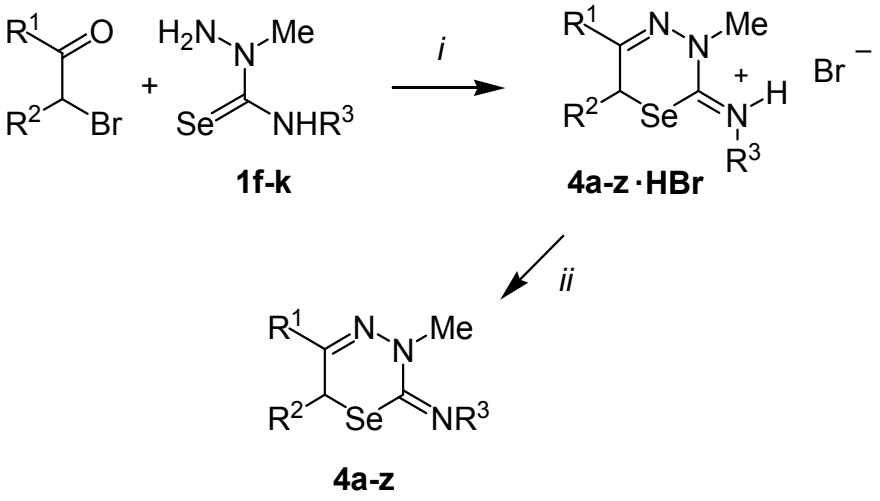
Scheme 3. Extrusion of selenium from **2**: *conditions*: AcOH, reflux, 1-24 h

Table 3. Extrusion of selenium from **2**

2	**5**	R^1	R^2	R^3	*t* [h]	Yield (%)[a]
a·HBr	**a**	Ph	Ph	Ph	2	93
b·HBr	**b**	Ph	Me	Ph	3	70
g	**c**	Ph	Ph	*t*Bu	1	55
h	**d**	Ph	Me	*t*Bu	4	79
o·HBr	**e**	Ph	Ph	Pr	2	73
p	**f**	Ph	Me	Pr	24	72
k·HBr	**g**	Ph	Ph	*i*Pr	3	69
l	**h**	Ph	Me	*iPr*	24	56

[a] Isolated yield

Cyclizations of 2-methyl-selenosemicarbazides. We earlier reported the cyclization of 2-methylselenosemicarbazides **1f-k** with phenacyl bromides.[8a,10] The compounds were only characterized by elemental analysis and (partly) by ^{1}H NMR and ^{77}Se NMR. Herein, we report the extension of the scope and the synthesis of the hydrobromides of 2-imino-3-methyl-2,3-dihydro-6*H*-1,3,4-selenadiazines **4a-aa** (Scheme 4, Table 4). Treatment of the latter with an aqueous solution of ammonia afforded the corresponding free bases. The products were additionally characterized by spectroscopic methods and by X-ray crystal structure analysis.



Scheme 4. Synthesis of 1,3,4-selenadiazines **4a-aa**: *conditions*: *i*, reflux, EtOH or *i*PrOH, 48% HBr; *ii*, aq. ammonia

Table 4. Synthesis of 1,3,4-selenadiazines **4a-aa**

4	R^1	R^2	R^3	% (**4**·HBr) [a]	% (**4**) [b]
a	Ph	Ph	Ph	52	100
b	Ph	Me	Ph	87	100
c	Ph	H	Ph	98	100
d	BrC_6H_4	H	Ph	57	100
e	ClC_6H_4	H	Ph	77	100
f	MeC_6H_4	H	Ph	99	100
g	Me	Ph	Ph	-	90
h	Me	Me	Ph	86	100
i	Ph	Ph	*t*Bu	58	100
j	Ph	Me	*t*Bu	96	100
k	Ph	H	*t*Bu	80	100
l	BrC_6H_4	H	*t*Bu	91	100
m	ClC_6H_4	H	*t*Bu	93	100
n	MeC_6H_4	H	*t*Bu	62	100
o	Ph	Ph	*i*Pr	62	100
p	Ph	Me	*i*Pr	75	100
q	Ph	H	*i*Pr	60	100

r	BrC_6H_4	H	*i*Pr	63	100
s	ClC_6H_4	H	*i*Pr	92	100
t	MeC_6H_4	H	*i*Pr	62	100
u	FC_6H_4	H	*i*Pr	95	100
v	Ph	Ph	*n*Pr	61	100
w	Ph	Me	*n*Pr	70	-
x	Ph	H	*n*Pr	92	95
y	ClC_6H_4	H	H	96	100
z	Ph	Ph	*s*Bu	58	-
aa	Me	H	Ph	71	-

[a] Yield of isolated hydrobromide. [b] Yield of isolated free base (based on **4**·HBr); for **2g**: yield of isolated free base (based on **1**)

Due to the presence of the methyl group located at the ring nitrogen atom, only the structure containing an exocyclic imino group is possible. The NMR data clearly show that all 1,3,4-selenadiazines **4a-aa** again reside in their 6*H*-form. The structure of **4p** was independently confirmed by X-ray crystal structure analysis (Figure 2).[11] Inspection of the crystal structure shows that **4p** exists in a twisted boat conformation. The structures of **4b**, **4d·HBr**, **4q·HBr**, and **4aa·HBr** were also studied by X-ray crystal structure analyses (Figures 3-6).[12] In all cases, a twisted boat conformation is observed. In case of the hydrobromides, the location of the H-atom attached to N3 was determined by difference electron density and refined freely. According to the molecular structure, the exocyclic and not the endocyclic imino group is protonated. The substituent R^3 points towards the selenium and not towards the methyl substituted endocyclic nitrogen atom, presumably due to steric reasons.

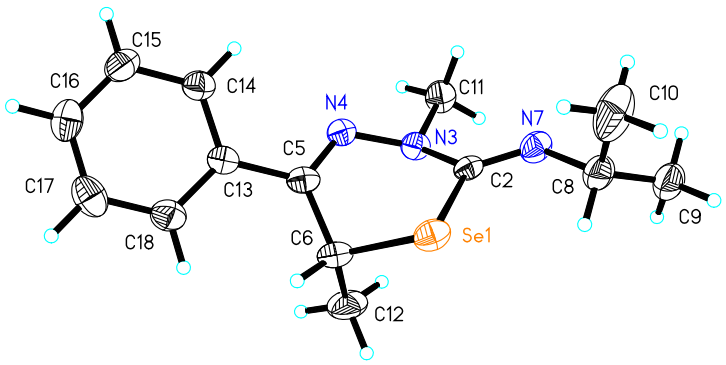


Figure 2. ORTEP plot of **4p** (50% probability level)

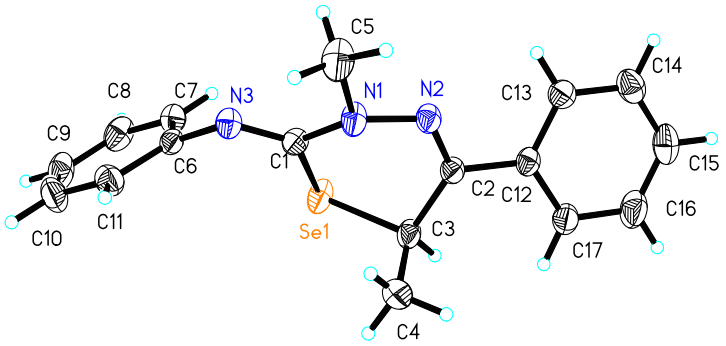


Figure 3. ORTEP plot of **4b** (50% probability level)

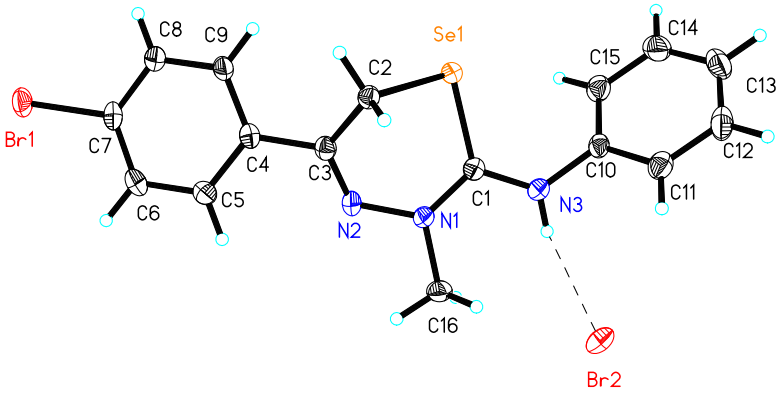


Figure 4. ORTEP plot of **4d·HBr** (50% probability level, the location of the H-atom located at N3 was determined by the difference electron density and refined freely)

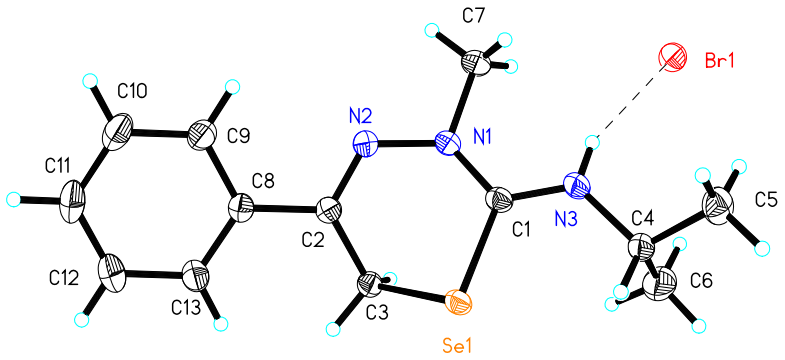


Figure 5. ORTEP plot of **4q·HBr** (50% probability level, the location of the H-atom located at N3 was determined by the difference electron density and refined freely)

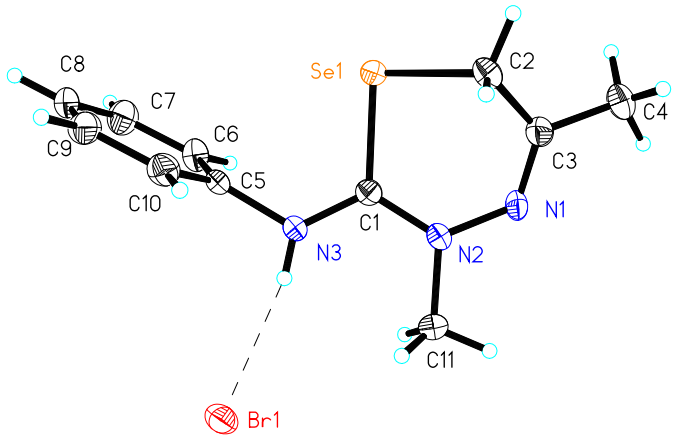
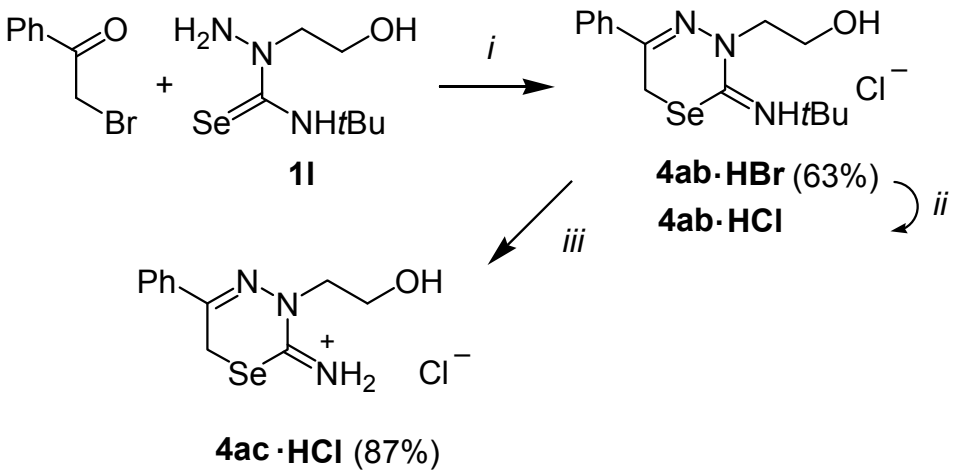


Figure 6. ORTEP plot of **4aa·HBr** (50% probability level, the location of the H-atom located at N3 was determined by the difference electron density and refined freely)

The cyclization of phenacyl bromide with 2-(2-hydroxyethyl)-selenosemicarbazide **1l** afforded 2-(*tert*-butyl)imino-3-(2-hydroxyethyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine **4ab** (Scheme 5). Reflux of **4ab** in conc. hydrochloric acid resulted in cleavage of the *tert*-butyl group and formation of **4ac** in the form of its hydrochloride. The structure of **4ac**·HCl was independently confirmed by X-ray crystal structure analysis (Figure 7).[11]



Scheme 5. Synthesis of 1,3,4-selenadiazines **4ab** and **4ac**: *conditions*: *i*, EtOH, 30 min, then reflux, 3 min; *ii*, HCl; *iii*, conc. HCl, reflux, 30 min

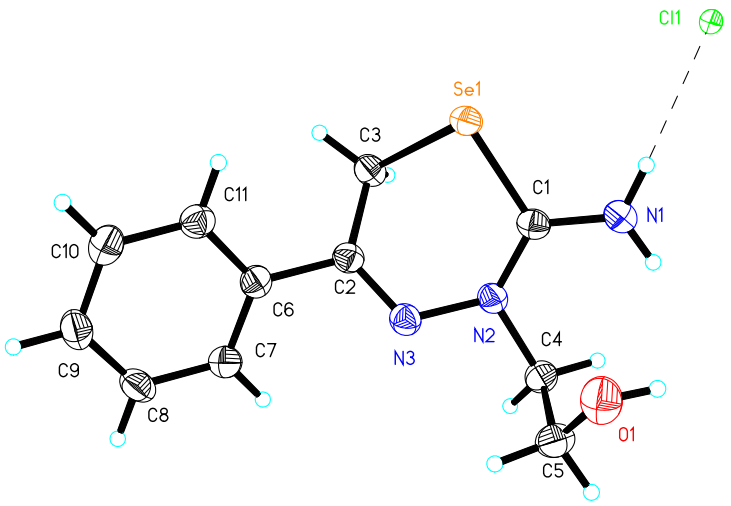
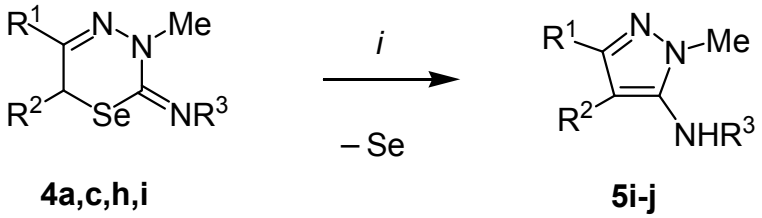


Figure 7. ORTEP plot of **4ac·HCl** (50% probability level, the location of the H-atom located at N3 was determined by the difference electron density and refined freely)

Reflux of a solution of 1,3,4-6*H*-selenadiazines **4c,g,h,i** in glacial acetic acid resulted in extrusion of selenium and formation of pyrazoles **5i-l** (Scheme 6, Table 5).[8a] The deselenation was already reported in our previous communications,[8a] but not all experimental details and data were provided. The formation of the products can be explained in analogy to the formation of **5a-h**.



4a,c,h,i **5i-j**

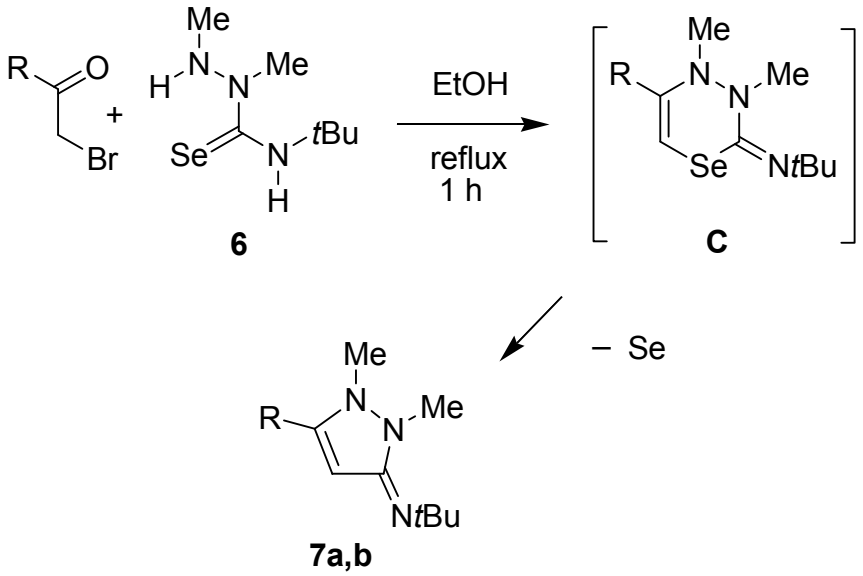
Scheme 6. Extrusion of selenium from **4a,c,h,i**: *conditions*: AcOH, reflux

Table 5. Extrusion of selenium from **4c,g,h,i**

4	**5**	R^1	R^2	R^3	Yield (%)[a]
c	**i**	Ph	H	Ph	74
g	**j**	Me	Ph	Ph	80
h	**k**	Me	Me	Ph	80
i	**l**	Ph	Ph	*t*Bu	95

[a] Isolated yield

Cyclizations of 1,2-dimethylselenosemicarbazides. The reaction of phenacyl bromides with 1,2-dimethylselenosemicarbazide **5**, containing methyl groups located at both nitrogen atoms of the hydrazine moiety, directly afforded the 5-imino-1,2-dimethylpyrazoles **7a** and **7b** in 54 and 62% yield, respectively (Scheme 7).[15] The formation of the products can be explained by formation of the unstable 1,3,4-4*H*-selenadiazines **C** which cannot be isolated because they undergo rapid extrusion of selenium following the mechanism as discussed for the formation of **5a-d**. While the deselenation of 1,3,4-selenadiazines 4 requires harsh and protic conditions (reflux of a solution of glacial acetic acid), the formation of **7a,b** proceeds under rather mild conditions (reflux, EtOH, 1 h). This can be explained as follows: in case of 1,3,4-6*H*-selenadiazines **4**, an isomerisation has first to take place to generate a 1,3,4-4*H* isomer (intermediate **A** in Scheme 6), while selenadiazine **C** already exists as 4*H* isomer. A rapid desulfurization has been previously reported for 1,3,4-4*H*-thiadiazines which represent thia analogues of **C**.[15]



Scheme 7. Cyclization of selenosemicarbazide **6** with α-phenacyl bromides (**7a**: R = C_6H_5, 54%, **7b**: R = 4'-ClC_6H_4: 62%)

In conclusion, we have reported the synthesis of various 1,3,4-selenadiazines by cyclization of selenosemicarbazides with phenacyl bromides. The compounds generally exist in their 6*H*-tautomeric form and contain an exocyclic imino group in the solid state. 1,3,4-4*H*-Selenadiazines, available from dimethylated selenosemicarbazides, cannot be isolated because they rapidly undergo a deselenation reaction under the conditions of their formation. Deselenation can be induced for 1,3,4-6*H*-selenadiazines under forcing conditions by reflux of a solution in glacial acetic acid. On the other hand, a ring contraction is observed when concentrated HCl or HBr is used.

EXPERIMENTAL

General. Reactions were carried out under inert atmosphere (Argon 4.6) in order to simultaneously exclude oxygen and water when appropriate. Pressure tubes were used to avoid condenser. Solvents for reactions were dried and distilled by standard methods or purchased from Merck®, Aldrich®, Acros Organics®, and others whenever exclusion of water was desired. Solvents for liquid chromatography and extraction were always distilled prior to use and partly reused after fractional distillation (*n*-heptane, ethyl acetate). NMR spectroscopy: ^{1}H NMR spectra (500.13 MHz and 300.13 MHz) and ^{13}C NMR spectra (125.8 MHz and 75.5 MHz) were recorded using Bruker spectrometers AVANCE 500 and AVANCE 300 with $CDCl_3$ as solvent. All chemical shifts are given in ppm and coupling constants in Hz. NMR spectra were calibrated using solvent signals ($CDCl_3$: d ^{1}H = 7.26, d ^{13}C = 77.0). The ^{1}H and ^{13}C NMR signals were assigned by DEPT and two-dimensional ^{1}H,^{1}H COSY, ^{1}H,^{1}H NOESY, and ^{1}H,^{13}C correlation spectra (HSQC and HMBC). Infrared Spectroscopy (IR): Nicolet 205 FT-IR, Nicolet Protége 460 FT-IR: Band intensities with the following assignments: *w* = weak, *m* = medium, *s* = strong, br = broad. Mass spectrometry (MS): AMD MS40, Varian MAT CH 7, MAT 731 (EI, 70 eV), Intecta AMD 402 (EI, 70 eV and CI), Finnigan MAT 95 (CI, 200 eV). High Resolution Mass Spectrometry (HRMS): Varian MAT 311, Intecta AMD 402. Elemental analysis (EA): LECO CHNS-932 Thermoquest Flash EA 1112. Melting Points: Micro heating table HMK 67/1825 Kuestner (Büchi Apparatus). Leitz Labolux 12 Pol with heating table Mettler FP 90. Melting points are uncorrected. X-ray crystal structure analysis: Bruker X8Apex Diffractometer with CCD-Kamera (Mo-K_a und Graphit Monochromator, λ = 0.71073 Å) or Bruker Apex Kappa-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073). Thin layer chromatography (TLC): Merck Kieselgel 60 F254 on aluminum foil from Macherey-Nagel. Detection was carried out under UV light at 254 nm and 365 nm. As colorizing reagent the following mixtures were used: 1-2/100 *p*-anisaldehyde or vanillin, 10/100 glacial acetic acid, 5/100 sulfuric acid, 83-84/100 MeOH. Column chromatography (CC): Merck Silica Gel 60 or Macherey-Nagel Silica Gel 60 (0.063-0.200 mm, 70-230 mesh). The finer Merck Silica Gel 60 (0.040-0.063 mm, 230-400 mesh) was chosen when appropriate.

General Procedure for the Synthesis of 2-Imino-5-aryl-6*H*-1,3,4-selenadiazines (2a-aa). *Hydrobromides*: An EtOH solution (20 mL) of selenosemicarbazide **1** (10.0 mmol) and of the phenacyl bromide (10.0 mmol) was stirred at 20 °C for 1 - 2 h. The mixture was heated under reflux for 5-10 min. The hot solution was filtered and the filtrate was cooled and slowly added to Et_2O (400 mL) with stirring and scratching the glass surface. A precipitate formed. In some cases the precipitate already formed when the reaction mixture was cooled. The solid was filtered off, washed with Et_2O/EtOH (9:1) and recrystallized from EtOH (for **2d-aa**) or EtOH/water (1:1, for **2a-c**) to give products **2a-aa** in the form of their

hydrobromides. *Free bases*: To an EtOH solution of the hydrobromide was added a diluted aqueous solution of ammonia until pH = 8 was reached. A precipitate formed which was filtered off and recrystallized from EtOH (for **2d-aa**) or from EtOH/water (1:1, for **2a-c**).

2-Phenylimino-5,6-diphenyl-6*H*-1,3,4-selenadiazine (2a). *Hydrobromide*: Yield: 3.49 g (74%), colorless solid (EtOH), mp 184 - 185 °C; IR (KBr, cm^{-1}): ν = 870 (w), 895 (w), 930 (w), 980 (w), 1018 (w), 1085 (m), 1191 (m), 1245 (m), 1315 (s), 1485 (s), 1545 (s), 1608 (s), 3080 (s), 3230 (s). *Anal.* Calcd for $C_{21}H_{18}N_3BrSe$ (471.27): C, 53.51; H, 3.85; N, 8.92. Found: C, 53.61; H, 3.91; N, 8.79. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 3.90 g (100%), light yellow prisms (EtOH), mp 192.5 - 194 °C; ^{1}H NMR (DMSO-d_6, 100 MHz): δ = 5.95 (s, 1H, 6-CH), 7.26 (m, 15H, ArH); due to the low solubility, a ^{13}C NMR spectrum could not be obtained. UV-Vis (EtOH, nm): λ_{max} (log ε) = 225 (4.47), 336 (4.15). *Anal.* Calcd for $C_{21}H_{17}N_3Se$ (390.35): C, 64.61; H, 4.39; N,10.76. Found: C, 69.50; H, 4.35; N, 10.75.

2-Phenylimino-5-phenyl-6-methyl-6*H*-1,3,4-selenadiazine (2b). *Free base*: Yield: 2.07 g (61%), light yellow prisms (*i*PrOH), mp 186 - 188 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.74 (d, 3H, 6-Me, *J* = 7.0 Hz), 4.72 (q, 1H, 6-CH, *J* = 4.3 Hz), 6.91 - 7.49 (m, 10H, ArH), 8.91 (s, 1H, NH). Due to the low solubility, a ^{13}C NMR spectrum could not be obtained. *Anal.* Calcd for $C_{16}H_{15}N_3Se$ (328.3): C, 58.54; H, 4.61; N, 12.80. Found: C, 58.61; H, 4.65; N, 12.91.

2-Phenylimino-5-phenyl-6*H*-1,3,4-selenadiazine (2c). *Free base*: Yield: 2.26 g (72%), yellow solid (EtOH), mp 181 - 183 °C; MS (EI, 70 eV): *m/z* = 315 (M^+, 88), 267 (89), 235 (3), 212 (42), 184 (51), 136 (58), 103 (100), 91 (4), 77 (17), 51 (2). Due to the low solubility, NMR spectra could not be obtained. *Anal.* Calcd for $C_{15}H_{13}N_3Se$ (314.25): C, 57.33; H, 4.17; N, 13.37. Found: C, 57.36; H, 4.20; N, 13.42.

2-Phenylimino-5-(4-bromophenyl)-6*H*-1,3,4-selenadiazine (2d). *Hydrobromide*: Yield: 4.08 g (86%), colorless prisms (EtOH), mp 200 - 201 °C. *Anal.* Calcd for $C_{15}H_{13}N_3Br_2Se$ (474.07): C, 38.00; H, 2.76; N, 8.86. Found: C, 38.00; H, 2.81; N, 8.87. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 3.93 g (100%), yellow needles (*i*PrOH), mp 184 °C; IR (KBr, cm^{-1}): ν = 905 (m), 986 (m), 1003 (m), 1162 (m), 1191 (m), 1215 (m), 1281 (m), 1410 (w), 1496 (m), 1566 (s), 1581 (s), 1621 (m), 2930 (m), 3080 (w), 3182 (w). Due to low solubility, NMR spectra could not be obtained. *Anal.* Calcd for $C_{15}H_{12}N_3BrSe$ (393.15): C, 45.83; H, 3.08; N, 10.69. Found: C, 45.81; H, 3.10; N, 10.71.

2-Phenylimino-5-(4-chlorophenyl)-6*H*-1,3,4-selenadiazine (2e). *Hydrobromide*: Yield: 1.95 g (56%),

colorless solid (EtOH), mp 195 - 197 °C; IR (KBr, cm^{-1}): ν = 1005 (m), 1098 (m), 1181 (w), 1231 (w), 1316 (m), 1380 (w), 1425 (m), 1461 (m), 1501 (s), 1586 (s), 1600 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.67 (s, 2H, 6-CH_2, ^2J (SeH) = 16.2 Hz), 6.93 - 7.71 (m, 9H, ArH), 9.22 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 15.6 (C6), 37.6, 121.8, 124.5, 127.6, 129, 133.8, 135.9, 147.3, 149.2, 151.7; ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 227. *Anal.* Calcd for $C_{15}H_{12}N_3ClSeBr$ (429.6): C, 41.94; H, 3.05; N, 9.78. Found: C, 41.81; H, 3.21; N, 9.79. *Free base*: Yield: 3.49 g (100%), yellow needles (*i*PrOH), mp 186 - 188 °C; UV-Vis (EtOH, nm): λ_{max} (log ε) = 231 (4.27), 334 (4.20); MS (EI, 70 eV): *m/z* = 349 (M^+, 52), 268 (8), 246 (78), 184 (77), 150 (11), 137 (99), 102 (54), 91 (22), 77 (100), 51 (48), 28 (33). Due to the low solubility, NMR spectra could not be obtained. *Anal.* Calcd for $C_{15}H_{12}N_3ClSe$ (348.7): C, 51.67; H, 3.47; N, 12.05. Found: C, 51.71; H; 3.51; N, 12.15.

2-Phenylimino-5-tolyl-6*H*-1,3,4-selenadiazine (2f). *Hydrobromide*: Yield 3.03 g (74%), colorless solid (EtOH), mp 192 - 193 °C; IR (KBr, cm^{-1}): ν = 1005 (w), 1198 (w), 1125 (w), 1321 (s), 1376 (m), 1426 (m), 1446 (m), 1500 (s), 1536 (s), 1581 (s), 1602 (s), 3005 (m), 3130 (w), 3180 (w). *Anal.* Calcd for $C_{16}H_{16}N_3BrSe$ (409.2): C, 52.70; H, 4.42; N, 10.27. Found: C, 52.71; H, 4.45; N, 10.30. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 3.28 g (100%), yellow solid (*n*BuOH), mp 184 - 186 °C; ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 2.35 (s, 3H, CH_3), 3.80 (s, 2H, 6-CH_2), 6.91 - 7.62 (m, 9H, ArH), 11.10 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ = 15.2, 20.8, 121.2, 123.6, 126.2, 128.7, 129.1, 132.7, 139.1, 147.6, 228.9; ^{77}Se NMR (DMSO-d_6, Me_2, Se): δ = 209.5. *Anal.* Calcd for $C_{16}H_{15}N_3Se$ (328.28): C, 58.54; H, 4.61; N, 12.80. Found: C, 58.61; H, 4.70; N, 12.74.

2-*tert*-Butylimino-5,6-diphenyl-6*H*-1,3,4-selenadiazine (2g). *Hydrobromide*: Yield: 3.38 g (85%), colorless prisms (EtOH, Et_2O), mp 184 - 185 °C; IR (KBr, cm^{-1}): ν = 1030 (w), 1080 (w), 1202 (s), 1320 (m), 1380 (m), 1405 (m), 1461 (m), 1502 (m), 1581 (s), 1624 (s), 2980 (s), 3185 (s). *Anal.* Calcd for $C_{19}H_{22}N_3Br_1Se_1$ (451.28): C, 50.57; H, 4.91; N, 9.31. Found: C, 50.61; H, 4.91; N, 9.47. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 3.70 g (100%), light yellow prisms (EtOH, H_2O), mp 192.5 - 194 °C; IR (KBr, cm^{-1}): ν = 980 (m), 1030 (w), 1081 (m), 1215 (s), 1270 (s), 1375 (s), 1460 (s), 1500 (s), 1545 (s), 1641 (s), 2980 (m), 3030 (m), 3070 (m); ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.40 (s, 9H, *t*Bu), 5.32 (s, 1H, 6-CH), 7.51 - 7.65 (m, 10H, ArH). Due to the low solubility, a ^{13}C NMR spectrum could not be obtained. *Anal.* Calcd for $C_{19}H_{21}N_3Se$ (370.36): C, 61.62; H, 5.72; N, 11.35. Found: C, 61.71; H, 5.81; N, 11.12.

2-*tert*-Butylimino-5-phenyl-6-methyl-6*H*-1,3,4-selenadiazine (2h). *Hydrobromide*: Yield: 3.11 g (80%),

colorless prisms (EtOH, Et_2O), mp 176 - 178 °C. *Anal.* Calcd for $C_{14}H_{20}N_3BrSe$ (389.21): C, 43.21; H, 5.18; N, 10.80. Found: C, 43.30; H, 5.24; N, 10.72. Due to the low solubility, NMR spectra could not be obtained. *Free Base*: Yield: 2.53 g (82%), light yellow prisms (EtOH, H_2O), mp 136 - 137 °C; IR (KBr, cm^{-1}): ν = 930 (w), 970 (m), 995 (m), 1030 (m), 1060 (m), 1221 (s), 1270 (s), 1380 (s), 1475 (s), 1540 (s), 2930 (m), 2980 (s), 3330 (m); ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.51 (s, 9H, *t*Bu), overlaped by 1.52 (d, 3H, 6-Me), 4.16 (q, 1H, 6-CH), 7.59 - 7.65 (m, 5H, ArH). Due to the low solubility, a ^{13}C NMR spectrum could not be obtained. *Anal.* Calcd for $C_{14}H_{19}N_3Se$ (308.29): C, 54.55; H, 6.21; N, 13.63. Found: C, 54.58; H, 6.30; N, 13.71.

2-(*tert*-Butyl)imino-5-phenyl-6*H*-1,3,4-selenadiazine (2i). *Hydrobromide*: Yield: 3.60 g (96%), colorless needles (EtOH), mp 220 - 221 °C; IR (KBr, cm^{-1}): ν = 905 (w), 1160 (m), 1205 (s), 1225 (m), 1306 (s), 1381 (s), 1401 (s), 1445 (s), 1538 (s), 1585 (s), 2905 (s), 2980 (s), 3030 (s), 3180 (s); ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 1.49 (s, 9H, *t*Bu), 4.22 (s, 2H, 6-CH_2, ^2J (SeH) = 14.7 Hz), 7.54 - 7.96 (m, 5H, ArH), 9.9 (s, 1H, NH), 12.8 (s, 1H, NH^+); ^{13}C NMR (DMSO-d_6, 300 MHz): δ = 18.3, 28.4, 56.1, 127.3, 129.1, 131.7, 132.6, 154.7, 213.1. *Anal.* Calcd for $C_{13}H_{18}$N3BrSe (375.18): C, 41.62; H, 4.84; N, 11.20. Found: C, 41.71; H, 4.91; N, 11.20. *Free base*: Yield: 2.94 g (100%), light yellow prisms (EtOH), mp 128 - 130 °C; IR (KBr, cm^{-1}): ν = 980 (s), 1071 (s), 1220 (s), 1265 (s), 1375 (s), 1390 (m), 1408 (m), 1460 (s), 1535 (s), 2980 (s), 3020 (s), 3205 (s); ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.52 (s, 9H, *t*Bu), 3.54 (s, 2H, 6-CH_2), 7.50 - 7.68 (m, 5H, ArH). Due to the low solubility, a ^{13}C NMR spectrum could not be obtained. *Anal.* Calcd for $C_{13}H_{17}N_3Se$ (294.26): C, 53.06; H, 5.82; N, 14.28. Found: C, 52.70; H, 5.80; N, 14.36.

2-(*tert*-Butyl)imino-5-(4-chlorophenyl)-6*H*-1,3,4-selenadiazine (2j). *Hydrobromide*: Yield: 3.11 g (76%), colorless solid, mp 220 - 221 °C. *Anal.* Calcd for $C_{13}H_{17}N_3BrClSe$ (409.62): C, 38.12; H, 4.18; N; 10.26. Found: C, 38.21; H, 4.25; N, 10.49. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, yellow prisms (EtOH), mp 132 - 134 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.50 (s, 9H, *t*Bu), 3.49 (s, 2H, 6-CH_2), 4.20 (s, 1H, NH), 7.50 - 7.65 (m, 4H, ArH). *Anal.* Calcd for $C_{13}H_{16}N_3ClSe$ (328.31): C, 47.50; H, 4.91; N, 12.78. Found: C, 47.62; H, 4.86; N, 12.75. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Isopropylimino-5,6-diphenyl-6*H*-1,3,4-selenadiazine (2k). *Hydrobromide*: Yield: 2.67 g (61%), colorless prisms (EtOH/ Et_2O), mp 213 - 213.5 °C; IR (KBr, cm^{-1}): ν = 950 (m), 1020 (m), 1040 (m), 1180 (m), 1295 (s), 1320 (s), 1450 (s), 1530 (s), 1590 (s), 1620 (s), 2980 (s), 3190 (s); ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 1.04 - 1.23 (m, 6H, *i*Pr), 3.35 - 3.49 (m, 1H, CH/H_2O), 4.25 (s, 2H, 6-CH_2), 7.33 - 7.87 (m, 10H, ArH), 10.25 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 21.4, 47.0, 126.7, 126.7, 128.6, 129.2, 129.3,

131.4, 133.5, 136.1, 152.1, 156.5; ^{77}Se NMR (DMSO-d_6, Me_2Se): δ = 403.9. *Anal.* Calcd for $C_{18}H_{20}N_3BrSe$ (437.25): C, 49.45; H, 4.61; N, 9.61. Found: C, 49.51; H, 4.70; N, 9.61. *Free base*: Yield: 2.17 g (61%), yellow prisms (EtOH/H_2O), mp 120 - 122 °C; IR (KBr, cm^{-1}): ν = 985 (m), 1035 (m), 1076 (m), 1128 (m), 1172 (s), 1245 (m), 1348 (m), 1371 (m), 1395 (m), 1460 (s), 1525 (s), 2980 (s), 3130 (m); ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.14 (d, 6H, *i*Pr), 4.33 (m, 1H, CH-*i*Pr), 5.39 (s, 1H, 6-CH), 7.40 - 7.61 (m, 10H, ArH). *Anal.* Calcd for $C_{18}H_{19}N_3Se$ (356.33): C, 60.67; H, 5.37; N, 11.79. Found: C, 60.81; H, 5.42; N, 12.01. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Isopropylimino-5-phenyl-6-methyl-6*H*-1,3,4-selenadiazine (2l). *Hydrobromide*: Yield: 2.73 g (78%), colorless prisms (EtOH/Et_2O), mp 212 °C; IR (KBr, cm^{-1}): ν = 995 (s), 1065 (m), 1137 (s), 1211 (m), 1278 (s), 1365 (s), 1455 (s), 1585 (s), 1620 (s), 2941 (s), 3121 (s). *Anal.* Calcd for $C_{13}H_{18}N_3BrSe$ (375.18): C, 41.62; H, 4.84; N, 11.20. Found: C, 41.73; H; 4.92; N, 11.32. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 2.94 g (100%), yellow prisms (EtOH), mp 147 - 148 °C; IR (KBr, cm^{-1}): ν = 960 (m), 995 (m), 1071 (m), 1125 (s), 1178 (s), 1202 (m), 1230 (s), 1315 (m), 1345 (s), 1370 (s), 1387 (s), 1445 (s), 1535 (s), 1595 (s), 1635 (s), 2920 (s), 3070 (s), 3180 (s); ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.26 (t, overlap by two doublets of the *i*Pr-Me group, 6H, *i*Pr), 1.58 (d, 3H, 6-Me), 4.24 (m, 2H, CH-*i*Pr and 6-CH), 7.62 (m, 5H, ArH). *Anal.* Calcd for $C_{13}H_{17}N_3Se$ (294.26): C, 53.06; H, 5.82; N, 14.28. Found: C, 53.12; H, 5.83; N, 14.42. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Isopropylimino-5-phenyl-6*H*-1,3,4-selenadiazine (2m). *Hydrobromide*: Yield: 3.47 g (96%), colorless solid (EtOH), mp 185 °C; IR (KBr, cm^{-1}): ν = 945 (m), 1080 (m), 1130 (m), 1185 (s), 1210 (m), 1311 (s), 1385 (m), 1398 (s), 1451 (s), 1530 (s), 1590 (s), 1620 (s), 2910 (s), 3030 (s), 3180 cm^{-1}. *Anal.* Calcd for $C_{12}H_{16}N_3BrSe$ (361.15): C, 39.91; H, 4.42; N, 11.64. Found: C, 39.87; H, 4.51; N, 11.75. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 2.80 g (100%), yellow rods (EtOH), mp 97.5 - 99 °C; IR (KBr, cm^{-1}): ν = 930 (s), 970 (m), 1020 (m), 1080 (m), 1132 (m), 1171 (s), 1230 (s), 1310 (m), 1350 (m), 1370 (m), 1390 (m), 1415 (m), 1450 (s), 1530 (s), 1580 (s), 1595 (s), 1645 (s), 2930 (s), 2980 (s), 3160 (s), 3180 (s); ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 1.18 (d, 6H, *i*Pr), 3.63 (s, 2H, 6-CH_2), 4.12 - 4.17 (s, 1H, CH, ^2J (SeH) = 13.4 Hz), 7.38 - 7.89 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 15.0, 21.9, 22.8, 45.4, 126.4, 128.5, 129.1, 144.2, 148.0; ^{77}Se NMR (DMSO-d_6, 75 MHz): δ = 148.8; ms (EI, 70 eV): *m/z* = 295 (M^+, 26), 239 (7), 212 (10), 197 (5), 159 (12), 131 (4), 117 (10), 103 (36), 77 (19), 57 (100), 41 (14). *Anal.* Calcd for $C_{12}H_{15}N_3Se_1$ (280.23): C, 51.43; H, 5.42; N, 14.99. Found: C, 51.20; H; 5.16; N, 14.79.

2-Isopropylimino-5-(4-chlorphenyl)-6*H*-1,3,4-selenadiazine (2n). *Hydrobromide*: Yield: 3.00 g (76%), colorless prisms (EtOH), mp 223 °C; ms (EI, 70 eV): *m/z* = 315 (M^+, 30), 246 (80), 220 (10), 193 (9), 169 (4), 149 (36), 137 (96), 107 (52), 101 (50), 77 (5), 76 (39), 43 (100), 41 (48). *Anal.* Calcd for $C_{12}H_{15}N_3BrClSe$ (395.6): C, 36.43; H, 3.82; N, 10.62. Found: C, 36.51; H, 3.76; N,10.86. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 3.14 g (100%), yellow prisms (EtOH), mp 145 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (d, 6H, *i*Pr, *J* = 6.2 Hz), 3.52 (s, 2H, 6-CH_2), 4.19 (m, 1H, CH, ^2J (SeH) = 15.5 Hz), 5.15 (s, 1H, NH); 7.51 - 7.66 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, Me_2Se): δ = 11.5, 15.4, 23.2, 47.2, 127.9, 128.7, 134.3, 135.5, 146.0, 147.8; ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 170.0. *Anal.* Calcd for $C_{12}H_{14}N_3Cl_1Se_1$ (314.68): C, 45.8; H, 4.48; N, 13.35. Found: C, 45.85; H, 4.42; N, 13.42.

2-(*n*-Propyl)imino-5,6-diphenyl-6*H*-1,3,4-selenadiazine (2o). *Hydrobromide*: Yield: 3.06 g (70%), colorless prisms (EtOH), mp 176 °C; IR (KBr, cm^{-1}): ν = 1180 (m), 1345 (s), 1461 (s), 1545 (s), 1605 (s), 2980 (s). *Anal.* Calcd for $C_{19}H_{20}N_3Br_1Se_1$ (437.25): C, 49.45; H, 4.61; N, 9.61. Found: C, 49.46; H, 4.71; N, 9.64. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, yellow prisms (EtOH), mp 105 - 106 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 0.80 (t, 3H, Me), 1.49 (m, 2H, CH_2), 3.41 (t, 2H, CH_2), 5.33 (s, 1H, 6-CH), 7.56 - 765 (m, 10H, ArH). *Anal.* Calcd for $C_{18}H_{19}N_3Se$ (356.33): C, 60.67; H, 5.37; N, 11.79. Found: C, 60.81; H, 5.41; N, 12.01. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-(*n*-Propyl)imino-5-phenyl-6-methyl-6*H*-1,3,4-selenadiazine (2p). *Hydrobromide:* Yield: 652 mg (87%), colorless prisms (EtOH), mp 192 - 192.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.00 (t, 2H, Pr-Me), 1.87 (m, 2H, CH_2), 2.23 (s, 3H, 5-Me), 3.35 (t, 3H, CH_2), 7.46 (m, 5H, ArH). *Anal.* Calcd for $C_{13}H_{18}Br_1N_3Se_1$ (375.17): C, 41.62; H, 4.84; N, 11.20. Found: C, 41,72; H, 4.72; N, 11.25. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained. *Free base*: Yield: 100%, light yellow rods (EtOH), mp 93.5 - 94 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 0.94 (t, 3H, Me-Pr), 1.57 (d, 3H, 6-Me), overlaped by 1.65 (m, 2H, CH_2), 3.52 (t, 2H, CH_2), 4.20 (q, 1H, 6-CH), 4.68 (s, 1H, NH), 7.62 (m, 5H, ArH). *Anal.* Calcd for $C_{13}H_{17}N_3Se_1$ (294.26): C, 53.06; H, 5.82; N, 14.28. Found: C, 53.16; H, 5.91; N, 1431. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-(*n*-Propyl)imino-5-phenyl-6*H*-1,3,4-selenadiazine (2q). *Hydrobromide*: Yield: 3.22 g (89%), colorless prisms (EtOH), mp 185 °C; IR (KBr, cm^{-1}): ν = 990 (m), 1070 (m), 1190 (m), 1161 (m), 1203 (s), 1325 (s), 1370 (m), 1415 (m), 1448 (s), 1480 (s), 1535 (s), 1595 (s), 1610 (s), 3040 (s), 3190 (s). *Anal.* Calcd for $C_{12}H_{16}N_3Br$ (361.15): C, 39.91; H, 4.47; N, 11.64. Found: C, 39.95; H, 4.81; N, 11.75. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, light yellow prisms (EtOH), mp

97.5 - 99 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.02 (t, 3H, Me), 1.68 (m, 2H, CH_2), 3.48 (t, 2H, CH_2), overlaped by 3.56 (s, 2H, 6-CH_2), 4.15 (s, 1H, NH), 7.50 - 7.63 (m, 5H, ArH). *Anal.* Calcd for $C_{12}H_{15}N_3Se$ (280.23): C, 51.43; H, 5.42; N, 14.99. Found: C, 51.45; H, 5.41; N, 14.81. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-(*n*-Propyl)imino-5-(4-chlorphenyl)-6*H*-1,3,4-selenadiazine (2r). *Free base*: Yield: 2.67 g (85%), yellow prisms (EtOH), mp 111 - 112 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.98 (s, 3H, CH_3), 1.61 - 1.74 (m, 2H, CH_2), 3.49 (m, 2H, N-CH_2), 3.52 (s, 2H, 6-CH_2, ^2J (SeH) = 14.1 Hz), 4.65 (s, 1H, NH), 7.37 - 7.82 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 11.47, 15.38, 23.23, 47.25, 127.95, 128.73, 134.31, 135.46, 147.82; ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 166.0. *Anal.* Calcd for $C_{12}H_{14}N_3Cl_1Se_1$ (314.68): C, 45.80; H, 4.48; N, 13.35. Found: C, 45.81; H, 4.51; N, 13.42.

2-Imino-5-(4-chlorophenyl-6*H*-1,3,4-selenadiazine (2s). *Free base*: Yield: 100%, yellow prisms ($EtOH/H_2O$), mp 68-69 °C; ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 3.59 (s, 2H, 6-CH_2, ^2J (SeH) = 16.0 Hz), 7.17 (s, 2H, NH_2), 7.41 - 8.31 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 14.94, 127.46, 128.26, 133.88, 135.06, 146.64, 147.28, ^1J (Se, C_6): 47 Hz; ^{77}Se NMR (DMSO-d_6, Me_2Se): δ = 147.0. *Anal.* Calcd for $C_9H_8N_3Cl_1Se$ (272.6): C, 39.65; H, 2.95; N, 15.41. Found: C, 39.71; H, 2.81; N, 1550.

Isolation of selenazoles 3a-d (method A). The side products were isolated in separate experiments as follows: To the crude reaction mixture [from selenosemicarbazide **1** (0.1 mmol) and phenacyl bromide (0.1 mmol)] was added an aqueous solution of ammonia (13.3 M, 15 mL). After standing, the solution was centrifugated to separate a small amount of selenium. The yellow solution was separated by syringe. The residue was washed twice with *i*PrOH (0.5 mL). The solution was purified by chromatography (sephadex LH_{20}, *i*PrOH). Besides **2**, by-products **3a-d** could be isolated.

2-Propylimino-4,5-diphenyl-2,3-dihydroselenazol-3-amine (3a). Method A: Yield: 4.9 mg (14%), light yellow prisms, mp 154 - 155 °C; IR (KBr, cm^{-1}): ν = 700 (s), 720 (m), 770 (M), 1090 (m), 1385 (s), 1451 (s), 1500 (m), 1635 (s), 2930 (m), 2980 (m). *Anal.* Calcd for $C_{18}H_{19}N_3Se$ (356.33): C, 60.67; H, 5.34; N, 11.79. Found: C, 60,71; H, 5.25; N, 11.65. Due to the low solubility, NMR spectra could not be obtained.

2-Isopropylimino-4,5-diphenyl-2,3-dihydroselenazol-3-amine (3b). Method A: Yield: 12.1 mg (34%), light yellow needles, mp 182 - 184 °C. *Anal.* Calcd for $C_{18}H_{19}N_3Se$ (356.33): C, 60.67; H, 5.34; N, 11.79. Found: C, 60,75; H, 5.35; N, 11.82. Due to the low solubility, NMR spectra could not be obtained.

2-Propylimino-4-phenyl-5-methyl-2,3-dihydroselenazol-3-amine (3c). Method A: Yield: 2.1 mg (7%), light yellow prisms (EtOH), mp 169 - 171 °C; IR (KBr, cm^{-1}): ν = 700 M), 780 (m), 1180 (m), 1250 (m) 1410 (s), 1530 (s), 2990 (m), 3380 (s), 3440 (s). *Anal.* Calcd for $C_{13}H_{17}N_3Se$ (294.26): C, 53.06; H, 5.82; N, 14.28. Found: C, 53,11; H, 5.85; N, 14.35. Due to the low solubility, ^{13}C NMR spectra could not be obtained. Method B: 588 mg (2 mmol) **2p** was refluxed in conc. HCl (5 mL). The mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in EtOH. Addition of Et_2O resulted in formation of a colourless precipitate of **3c·HCl**. Yield: 400 mg (60%). Colourless prisms (EtOH/Et_2O); mp 227 - 229 °C. *Anal.* Calcd for $C_{13}H_{18}Cl_1N_3Se_1$ (330.72): C, 47.21; H, 5.48; N, 12.72. Found: C, 47,22; H, 5.52; N, 12.75. Method C: 750 mg (2mmol) of **2p·HBr** was heated for 30 min in conc. HBr (5 mL). Work up as described in method B gave **3c·HBr**; ^1H NMR ($CDCl_3$ 100 MHz): δ = 1.00 (s, 3H, Pr-Me); 1.87 (m, 2H, CH_2); 2.23 (s, 3H, 5-Me); 3.35 (t, 2H, CH_2); 7.46 (m 6H, Ph). Yield: 650 mg (87%). *Anal.* Calcd for $C_{13}H_{18}Br_1N_3Se_1$ (375.17): C, 41.62; H, 4.84; N, 11.20. Found: C, 41,72; H, 4.72; N, 11.25.

2-Isopropylimino-4-phenyl-5-methyl-2,3-dihydroselenazol-3-amine (3d). Method A: Yield: 5.1 mg (17%), light yellow needles (EtOH/Et_2O), mp 118.5 - 119.5 °C; ^1H NMR ($CDCl_3$, 100 MHz): δ = 1.23 (d, 6H, *i*Pr-Me), 2.09 (s, 3H, 5-Me), 3.02 (m, 1H, *i*PrCH), 4,22 (s, 2H, NH_2), 7.30 (m, 5H, ArH). *Anal.* Calcd for $C_{13}H_{17}N_3Se$ (294.26): C, 53.06; H, 5.82; N, 14.28. Found: C, 53,21; H, 5.87; N, 14.32. Method B: 294 mg (1 mmol) of **2l** were heated for 2.5 h in conc. HCl (10 mL) under reflux. Cooling resulted in precipitation of **3d·HCl**. Yield: 220 mg (67%); colourless prisms (EtOH/Et_2O), mp 196 - 197 °C. *Anal.* Calcd for $C_{13}H_{18}Cl_1N_3Se_1$ (330.72): C, 47.21; H, 5.48; N, 12.72. Found: C, 47,23; H, 5.50; N, 12.74. Method C: 750 mg (2 mmol) of **2l·HBr** were heated for 30 min in conc. HBr (5 mL) under reflux. The solution was cooled and concentrated to give **3d·HBr**. Yield 690 mg (92%); colourless prisms (EtOH/Et_2O); mp 192.5 - 193 °C. *Anal.* Calcd for $C_{13}H_{18}Br_1N_3Se_1$ (375.17): C, 41.62; H, 4.84; N, 11.20. Found: C, 41,73; H, 4.74; N, 11.26.

General Procedure for the Synthesis of 2-Imino-3-methyl-2,3-dihydro-6*H*-1,3,4-selenadiazines (4a-aa). *Hydrobromides:* To an EtOH solution (10 - 20 mL) of selenosemicarbazide **1** (10.0 mmol) was dropwise added an EtOH solution (10 mL) of the phenacyl bromide (10.0 mmol) at 0 °C with vigorous stirring. The mixture was stirred for 1 h and then refluxed for 10 min. Subsequently, the solution was filtered and the filtrate was cooled to 0 °C. To the solution was slowly added Et_2O with stirring and scratching of the glass surface. A precipitate formed which was recrystallized from EtOH. *Free bases*: To an EtOH solution of the pure hydrobromide was slowly added a dilituted aqueous solution of ammonia until pH = 8 was reached. A precipitate formed which was filtered off and recrystallized from EtOH.

2-Phenylimino-3-methyl-5,6-diphenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4a). *Hydrobromide*: Yield:

2.52 g (52%), colorless prisms (EtOH/Et_2O) mp 189 °C; IR (KBr, cm^{-1}): ν = 935 (w), 1030 (w), 1080 (w), 1236 (m), 1451 (m), 1480 (m), 1500 (m), 1548 (s), 1600 (m), 2930 (m), 3130 (w); ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 3.80 (s, 3H, N-Me), 6.08 (s, 1H, 6H, ^2J (SeH) 29.3 Hz), 7.17 - 7.80 (m, 15H, ArH), 8.34 (s, 1H, NH^+); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 36.57 (C_6), 43.72, 124.84, 126.44, 126.81, 126.88, 127.4, 128.33, 128.98, 129.21, 129.45, 131.11, 136.5, 141.53, 150.28, 256.42. ^1J (Se, C_6) 55.9; ^{77}Se NMR (DMSO-d_6), Me_2Se) 397; ms (EI, 70 eV): *m/z* = 405 (M^+, 4), 251 (4), 221 (7), 210 (8), 149 (3), 105 (100), 77 (36), 51 (10), 43 (6). *Anal.* Calcd for $C_{22}H_{20}N_3Br_1Se_1$ (485.29): C, 54.45; H, 4.15; N, 8.66. Found: C, 54.46; H, 4.18; N, 6.85. *Free base*: Yield: 100%, yellow prisms (EtOH), mp 101 °C; IR (KBr, cm^{-1}): ν = 930 (m), 1016 (m), 1080 (m), 1180 (m), 1200 (m), 1221 (m), 1239 (m), 1305 (m), 1446 (m), 1500 (m), 1581 (s), 2930 (w), 3025 (w), 3076 (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.82 (s, 3H, N-Me), 5.28 (s, 1H, 6-CH, ^2J (SeH) 9.4 Hz), 6.73 - 7.75 (m, 15H, ArH); ^{13}C NMR ($CDCl_3$, 300 MHz) δ = 35.6, 43.4, 121.98, 123.79, 126.19, 127.1, 127.60, 128.48, 128.57, 128.79, 129.25, 136.2, 137.89, 144.84, 145.87, 150.25. ^1J (Se,C_6) 55.9 Hz; ^{77} Se NMR (DMSO-d_6, Me_2Se): δ = 396.0; MS (EI, 70 eV): *m/z* = 405 (M^+, 5), 251 (5), 221 (7), 210 (10), 179 (10), 149 (4), 105 (100), 77 (38), 51 (8). Anal. Cald. for $C_{22}H_{19}N_3Se_1$ (404.38): C, 65.35; H, 4.74; N, 10.39. Found: C, 65.36; H, 4.78; N, 1057.

2-Phenylimino-3,6-dimethyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4b). *Hydrobromide*: Yield: 3.68 g (87%), coloress prisms (EtOH), mp 186 °C. *Anal.* Calcd for $C_{17}H_{18}N_3Br_1Se_1$ (423.22): C, 48.25; H, 4.29; N, 9.93. Found: C, 48.38; H, 4.30; N, 9.64. Due to the low solubility, NMR spectra could not be obtained. *Free base*: 100%, light yellow needles (EtOH), mp 128 °C; IR (KBr, cm^{-1}): ν = 916 (m), 982 (m), 1009 (m), 1045 (m), 1080 (m), 1100 (m), 1200 (m), 1226 (s), 1271 (m), 1301 (s), 1442 (s), 1495 (m), 1582 (s), 2925 (w), 3030 (w), 3060 (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.70 (d, 3H, Me, *J*= 7.3 Hz), 3.80 (s, 3H, N-Me), 4.57 - 4.66 (q, 1H, CH, *J* = 7.2 Hz, ^2J (SeH), 37.8 Hz), 6.86 - 7.76 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.7, 26.7 (C_6), 43.5, 122.2, 123.9, 126, 128.7, 129.4, 135.4, 147.1, 148.1, 150.6 (^1J (Se, C_6) = 58.16 Hz). ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 327.0; uv (EtOH): λ_{max} (log ε) = 229 (4.19), 336 (4.11); MS (EI, 70 eV): *m/z* = 343 (M^+, 28), 240 (3), 183 (3), 160 (16), 117 (100), 91 (10), 77 (9), 51 (3). *Anal.* Calcd for $C_{17}H_{17}N_3Se_1$ (342.3): C, 59.65; H, 5.01; N, 12.28. Found: C, 59.71; H, 5.20; N, 12.38.

2-Phenylimino-3-methyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4c).

Hydrobromide: Yield: 4.01 g (98%), colorless prisms (EtOH), mp 198 °C; IR (KBr, cm^{-1}): ν = 1025 (w), 1081 (w), 1165 (w), 1192 (w), 1235 (s), 1321 (s), 1385 (s), 1415 (s), 1451 (s), 1481 (s), 1500 (s), 1553 (s), 1600 (s), 2900 (s), 3030 (s), 3105 (m). *Anal.* Calcd for $C_{16}H_{16}N_3Br_1Se_1$ (409.2): C, 46.96; H, 3.94; N, 10.27. Found: C, 46.91; H, 3.96; N, 10.16. Due to the low solubility, NMR spectra could not be obtained. *Free*

base: Yield: 100%, light yellow solid (EtOH), mp 95 °C; IR (KBr): ν = 930 (m), 1025 (m), 1041 (m), 1066 (m), 1192 (m), 1221 (s), 1291 (s), 1408 (m), 1441 (m), 1496 (m), 1582 (s), 2930 (w), 3130 (w), 3181 (w); ^{1}H NMR (DMSO-*d*$_6$, 300 MHz): δ = 3.63 (s, 3H, N-Me), 3.90 (s, 2H, 6-CH_2, ^{2}J (SeH) = 15 Hz), 6.79 - 7.95 (m, 10H, ArH); ^{13}C NMR (DMSO-*d*$_6$, 75 MHz): δ = 15.8 (C_6), ^{1}J (Se, C_6) 51.9 Hz, 42.8, 121.8, 123.6, 126.2, 128.6, 128.7, 129.7, 134.6, 149.4, 151 (C_2), 151.8; ^{77}Se NMR (DMSO-*d*$_6$, Me_2Se): δ = 240.0; uv-vis (EtOH): λ_{max} (log ε) = 234 (4.22), 338 (4.04), MS (EI, 70 eV): *m/z* = 329 (M^+, 22), 226 (19), 183 (6), 146 (5), 117 (4), 103 (100), 77 (10), 51 (3), 43 (4). *Anal.* Calcd for $C_{16}H_{15}N_3Se_1$ (328.28): C, 58.54; H, 4.61; N, 12.80. Found: C, 58.61; H, 4.70; N, 12.71.

2-Phenylimino-3-methyl-5-(4-bromophenyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4d).

Hydrobromide: Yield: 2.78 g (57%), colorless prisms (EtOH), mp 215 - 216 °C; IR (KBr): ν = 945 (m), 1010 (m), 1086 (m), 1150 (w), 1195 (w), 1235 (m), 1320 (m), 1380 (s), 1431 (s), 1490 (s), 1563 (s), 1598 (s), 2900 (s), 3030 (m), 3100 (m) cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$, 200 MHz): δ = 3.69 (s, 3H, N-Me), 3.94 (s, 2H, 6-CH_2), 5.58 (s, 1H, NH^+), 6.95 - 7.85 (m, 9H, ArH, ^{2}J (SeH) = 15 Hz); ^{13}C NMR (DMSO-*d*$_6$, 50 MHz): δ = 17.47, 43.16, 124.13, 124.38, 126.65, 128.80, 129.17, 131.81, 132.63, 151.31. *Anal.* Calcd for $C_{16}H_{15}N_3Br_2Se_1$ (488.1): C, 39.37; H, 3.10; N, 8.61. Found: C, 39.41; H, 3.12; N, 8.48. *Free base*: Yield: 100%, light yellow lamella (EtOH), mp 118 °C; IR (KBr, cm^{-1}): ν = 930 (m), 1008 (m), 1030 (m), 1070 (m), 1081 (m), 1135 (w), 1180 (w), 1200 (m), 1225 (s), 1230 (s), 1290 (s), 1490 (m), 1495 (s), 1594 (s), 2930 (w), 3070 (w); ^{1}H NMR (DMSO-*d*$_6$, 300 MHz): δ = 3.63 (s, 3H, N-Me), 3.89 (s, 2H, 6-CH_2, ^{2}J (SeH) = 15 Hz), 6.79 - 7.80 (m, 9H, ArH); ^{13}C NMR (DMSO-*d*$_6$, 75 MHz): δ = 15 (C_6), 42.92, 121.5, 123.23, 123.74, 128.2, 128.8, 131.8, 148.1, 150.9, 151.5, ^{1}J (Se, C_6) 51.7 Hz; ^{77} Se NMR (DMSO-*d*$_6$, Me_2Se): δ = 237.0; uv (EtOH): λ_{max} (log ε) 428 (4.19), 344 (4.06). *Anal.* Calcd for $C_{16}H_{14}N_3Br_1Se$ (407.2): C, 47.20; H, 3.47; N, 10.32. Found: C, 47.25; H, 3.49; N, 10.18.

2-Phenylimino-3-methyl-5-(4-chloromethyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4e).

Hydrobromide: Yield: 3.41 g (77%), colorless rods (EtOH), mp 207.5 °C, IR (KBr, cm^{-1}): ν = 945 (m), 1015 (m), 1095 (s), 1160 (m), 1198 (m), 1235 (m), 1331 (m), 1396 (m), 1430 (m), 1491 (s), 1500 (s), 1568 (s), 1600 (s), 2900 (s), 3020 (m), 3105 (m); MS (EI, 70 eV): *m/z* = 363 (M^+, 32), 260 (27), 217 (3), 183 (6), 151 (3), 137 (100), 131 (7), 101 (11), 77 (10), 65 (3), 43 (5). *Anal.* Calcd for $C_{16}H_{15}N_3Cl_1Br_1Se_1$ (443.63): C, 43.32; H, 3.40; N, 9.47; Se, 17.80. Found: C, 43.41; H, 3.50; N, 9.38; Se, 18.11. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, light yellow lamella (EtOH), mp 123 °C, IR (KBr, cm^{-1}): ν = 930 (m), 1010 (m), 1097 (m), 1180 (m), 1200(m), 1225 (s), 1290 (s), 1405 (s), 1595 (s), 2930 (s), 3170 (w) cm^{-1}; MS (EI, 70 eV): *m/z* = 363 (M^+, 31), 260 (28), 217 (6), 183 (8), 137 (100), 131 (6),

77 (10), 43 (5); uv (EtOH): λ_{max} (log ε) = 242 (4.21), 340 (4.08). *Anal.* Calcd for $C_{16}H_{14}N_3Cl_1Se_1$ (362.72): C, 52.98; H, 3.89; N, 11.58; Se, 21.77. Found: C, 52.91; H, 3.72; N, 11.42. Due to the low solubility, NMR spectra could not be obtained.

2-Phenylimino-3-methyl-5-tolyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4f). *Hydrobromide*: Yield: 4.19 g (99%), colorless rods (EtOH), mp 205 - 206 °C; IR (KBr, cm^{-1}): ν = 930 (m), 1140 (m), 1198 (m), 1236 (m), 1318 (m), 1416 (m), 1471 (m), 1500 (m), 1535 (s), 1600 (m), 2930 (m), 3020 (m), 3080 (m); ^{1}H NMR (DMSO-d_6, 200 MHz): δ = 1.96 (s, 3H, Me), 3.99 (s, 2H, 6-CH_2), 5.69 (s, 1H, NH^+), 7.12 - 7.84 (m, 9H, ArH); ^{13}C NMR (DMSO-d_6, 50 MHz): δ = 17.57, 20.87, 43.01, 124.27, 126.84, 129.19, 12 9.4, 130.46, 140.70, 140.83, 152.66. *Anal.* Calcd for $C_{17}H_{18}N_3Br_1Se$ (423.22): C, 48.25; H, 4.29; N, 9.93. Found: C, 48.32; H, 4.28; N, 9.69. *Free base*: Yield: 100%, light yellow prisms (EtOH), mp 100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.39 (s, 3H, Me), 3.61 (s, 2H, 6-CH_2, ^2J (SeH) = 15.6 Hz), 3.74 (s, 3H, N-Me), 7.29 - 7.67 (m, 9H, ArH), ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 15.85 (C_6), 21.3, 43.2, 121.9, 124, 126.3, 128.8, 129.4, 132.4, 139.9, 149, 151.6 (C_2), ^1J (Se, C_6) = 51.7 Hz ,^1J (Se, C_2) = 136 Hz; ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 246.0, uv-vis (EtOH): λ_{max} (log ε) = 232 (4.25), 336 (4.11), MS (EI, 70 eV): *m/z* = 343 (M^+, 18), 240 (15), 183 (3), 131 (5), 117 (100), 91 (10), 77 (5), 65 (3). *Anal.* Calcd for $C_{17}H_{17}N_3Se_1$ (342.31): C, 59.65; H, 5.01; N, 12.28. Found: C, 59.63; H, 5.12; N, 12.38.

2-Phenylimino-3,5-dimethyl-6-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4g). *Free base*: Yield: 3.08 g (90%), yellow prisms (EtOH), mp 95 - 97 °C, ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.02 (s, 3H, Me), 3.62 (s, 3H, N-Me), 4.68 (s, 1H, 6-CH), 6.79 - 7.38 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$), 50 MHz): δ = 22.11, 38.58, 42.27, 121.85, 123.87, 128.03, 128.31, 128.82, 136.10, 151.26, 151.82. *Anal.* Calcd for $C_{17}H_{17}N_3Se$ (342.3): C, 59.65; H, 5.01; N, 12.28. Found: C, 59.71, H, 5.22; N, 12.31.

2-Phenylimino-3,5,6-trimethyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4h). *Hydrobromide*: Yield: 3.01 g (86%), colorless needles (EtOH), mp 201.5 - 202 °C. *Anal.* Calcd for $C_{12}H_{16}N_3Br_1Se_1$ (361.14): C, 39.91; H, 4.47; N, 11.64. Found: C, 39.80; H, 4.51; N, 11.71. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless prims (EtOH): mp 47 °C; MS (EI, 70 eV): *m/z* = 281 (M^+, 58), 184 (6), 132 (12), 98 (45), 77 (10), 55 (100), 43 (5). *Anal.* Calcd for $C_{12}H_{15}N_3$ (280.23): C, 51.43; H, 5.40; N, 14.99. Found: C, 51.48; H, 5.45; N, 14.81. Due to the low solubility, NMR spectra could not be obtained.

2-*tert*-Butylimino-3-methyl-5,6-diphenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4i).

Hydrobromide: Yield: 2.70 g (58%), light yellow prisms (EtOH), mp 128 - 130 °C; IR (KBr): ν = 901 (w),

1030 (w), 1080 (w), 1198 (s), 1235 (m), 1315 (m), 1350 (m), 1380 (s), 1410 (s), 1450 (m), 1491 (s), 1571 (s), 2940 (s), 2980 (s), 3180 (m) cm^{-1}. *Anal.* Calcd for $C_{20}H_{24}N_3Br_1Se_1$ (465.30): C, 51.63; H, 5.20; N, 9.03. Found: C, 51.81; H, 5.25; N, 9.10. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless prisms ($EtOH/H_2O$) mp 77.5 °C; IR (KBr, cm^{-1}): ν = 830 (w), 905 (m), 930 (m), 1015 (m), 1080 (s), 1205 (s), 1240 (s), 1280 (m), 1380 (m), 1395 (m), 1450 (m), 1500 (s), 2910 (m), 2980 (s), 3030 (w), 3080 (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.17 (s, 9H, *t*Bu), 3.54 (s, 3H, NCH_3), 5.21 (s, 1H, 6-CH), 7.54 - 7.93 (m, 10H, ArH). *Anal.* Calcd for $C_{20}H_{23}N_3Se_1$ (384.39): C, 62.50; H, 6.03; N, 10.93. Found: C, 62.30; H, 6.12; N, 10.81. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-*tert*-Butylimino-3,6-dimethyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4j).

Hydrobromide: Yield: 3.87 g (96%), colorless rods (EtOH) mp 227 °C; IR (KBr): ν = 830 (w), 890 (w), 925 (w), 995 (w), 1025 (w), 1075 (m), 1105 (m), 1206 (s), 1345 (s), 1381 (s), 1410 (s), 1460 (s), 1494 (s), 1570 (s), 2981 (s), 3202 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 1.56 (s, 9H, *t*Bu), 1.63 (s, 3H, Me), 3.86 (s, 3H, N-Me), 4.54 - 4.56 (q, 1H, 6-CH, ^2J (SeH) 21.1 Hz), 7.42 - 7.79 (m, 5H, ArH), 8.54 (s, 1H, NH^+); ^{77}Se NMR (DMSO-d_6, Me_2Se) 395. *Anal.* Calcd for $C_{15}H_{22}N_3Br_1Se_1$ (403.23): C, 44.68; H, 5.50; N, 10.42. Found: C, 44.71; H, 5.51; N, 10.70. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained. *Free base*: Yield: 100%, colorless rods (EtOH), mp 65 °C; IR (KBr, cm^{-1}): ν = 895 (w), 930 (w), 990 (m), 1001 (s), 1008 (s), 1031 (s), 1085 (s), 1094 (s), 1215 (s), 1285 (s), 1378 (s), 1451 (s), 1500 (m), 1602 (s), 2990 (s), 3190 (w); ^{1}H NMR (DMSO-d_6, 300 MHz) δ = 1.29 (s, 9H, *t*Bu), 1.62 (d, 3H, 6-CH_3), 3.44 (s, 3H, N-Me), 4.54-4.56 (q, 1H, 6-CH, ^{2}J (SeH) 36.21 Hz), 7.40 -7.77 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 18.86 (C6), 26.56, 29.98, 43.42, 53.73, 125.52, 128.56, 128.99, 135.07, 139.01, 147.44; ^{77}Se NMR (DMSO-d_6, Me_2 Se): δ = 336.0; MS (EI, 70 eV): *m/z* = 323 (M^+, 4), 240 (22), 160 (20), 145 (5), 117 (100), 91 (4), 77 (3), 57 (18). *Anal.* Calcd for $C_{15}H_{21}N_3Se$ (322.32): C, 55.90; H, 6.57; N, 13.04. Found: C, 55.94; H, 6.65; N, 13.06.

2-*tert*-Butylimino-3-methyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selnadiazine (4k).

Hydrobromide: Yield: 3.11 g (80%), colorless prisms ($EtOH/Et_2O$), mp 220 - 221 °C, IR (KBr, cm^{-1}): ν = 1030 (w), 1085 (w), 1170 (m), 1202 (s), 1255 (m), 1310 (s), 1381 (s), 1411 (s), 1445 (m), 1498 (s), 1571 (s), 2980 (s), 3170 (m); ^{1}H NMR (DMSO-d_6, 300 MHz) δ = 1.56 (s, 9H, *t*Bu), 3.80 (s, 3H, N-Me), 4.27 (s, 2H, 6-CH_2, ^2J (SeH) = 14.9 Hz), 7.54 - 7.98 (m, 5H, ArH), 8.58 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ = 19.85, 29.27, 42.92, 56.69, 126.64, 127.43, 128.46, 129.19, 131.78, 131.98, 157.04, 164.35. ^{77}Se NMR (DMSO-d_6, Me_2Se) 264.7. *Anal.* Calcd for $C_{14}H_{20}N_3Br_1Se_1$ (389.21): C, 43.21; H, 5.18; N, 10.80. Found: C, 43.12; H, 5.20; N, 10.84. *Free base*: Yield: 100%, colorless prisms ($EtOH/H_2O$), mp 44 °C, IR (KBr, cm^{-1}):

ν = 1008 (s), 1115 (w), 1130 (w), 1205 (s), 1331 (w), 1372 (s), 1412 (m), 1445 (m), 1605 (s), 2930 (m), 2980 (s); ^{1}H NMR (DMSO-d_6, 300 MHz) δ = 1.27 (s, 9H, *t*Bu), 3.33 (s, 3H, N-Me), 3.90 (s, 2H, 6-CH_2), 7.41 - 7.82 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6, 300 MHz) δ = 16.17, 29.47, 43.16, 53.5, 126.02, 128.5, 129.52, 134.71, 144.15, 151.12; ^{77}Se NMR (DMSO-d_6, Me_2Se): δ = 264.7. *Anal.* Calcd for $C_{14}H_{19}N_3Se_1$ (308.29): C, 54.55; H, 6.21; N, 13.63. Found: C, 54.51; H, 6.22; N, 13.68.

2-*tert*-Butylimino-3-methyl-5-(4-bromophenyl)-6*H*-1,3,4-selenadiazine (4l). *Hydrobromide*: Yield: 4.26 g, 91%, colorless rods (EtOH/Et_2O), mp 191 °C; IR (KBr, cm^{-1}): ν = 1015 (m), 1085 (m), 1158 (s), 1221 (m), 1320 (s), 1381 (s), 1410 (s), 1497 (s), 1591 (s), 2480 (m), 3210 (m); MS (EI, 70 eV): *m/z* = 387 (M^+, 8), 372 (5), 304 (100), 260 (5), 225 (4), 181 (91), 102 (45), 77 (69, 57 (96), 41 (20). Due to the low solubility, NMR spectra could not be obtained. *Anal.* Calcd for $C_{14}H_{19}N_3Br_2Se_1$ (468.10): C, 35.92; H, 4.09; N, 8.98. Found: C, 35.81; H, 4.20; N, 8.88. *Free base*: Yield: 100%, colorless lamella (EtOH), mp 52.5 °C; IR (KBr, cm^{-1}): ν = 1008 (s), 1091 (m), 1208 (s), 1376 (m), 1415 (m), 1498 (m), 1610 (s), 3080 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.30 (s, 9H, *t*Bu), 3.43 (s, 3H, N-CH_3), 3.66 (s, 2H, 6-CH_2, ^{2}J (SeH) 15.3 Hz), 7.50 - 7.61 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 15.8 (C_6), 29.7 (Me, *t*Bu), 43.8, 54.1, 123.6, 127.5, 131.7, 134.4, 142 (C_2), 142.8 (^{1}J (SeC_6) = 54.1 Hz, ^{1}J (SeC_2) = 15.1 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 263.0; MS (EI, 70 eV): *m/z* = 387 (M^+, 8), 372 (5), 304 (100), 260 (5), 225 (4), 181 (91), 102 (45), 77 (6), 57 (96), 41 (20). *Anal.* Calcd for $C_{14}H_{18}N_3Br_1Se_1$ (387.19): C, 43.43; H, 4.69; N, 10.85. Found: C, 43.52; H, 4.72; N, 10.85.

2-*tert*-Butylimino-3-methyl-5-(4-chlorophenyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4m). *Hydrobromide*: Yield: 3.93 g (93%), colorless needles (EtOH/Et_2O), mp 190.5 °C; IR (KBr, cm^{-1}): ν = 1010 (s), 1042 (w), 1085 (m), 1098 (s), 1155 (m), 1205 (s), 1255 (m), 1315 (s), 1381 (s), 1415 (s), 1495 (s), 1582 (s), 2980 (s), 3201 (s). *Anal.* Calcd for $C_{14}H_{19}N_3Br_1Cl_1Se_1$ (423.65): C, 39.69; H, 4.52; N, 9.92. Found: C, 39.75; H, 4.61; N, 9.81. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless prisms (EtOH), mp 40.5 °C; IR (KBr, cm^{-1}): ν = 931 (m), 1015 (s), 1070 (s), 1100 (s), 1138 (m), 1215 (s), 1331 (m), 1378 (s), 1416 (s), 1502 (s), 1605 (s), 2980 (s); ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.30 (s, 9H, *t*Bu), 3.44 (s, 3H, N-Me), 3.63 (s, 2H, 6-CH_2), 7.57 - 7.64 (m, 4H, ArH). *Anal.* Calcd for $C_{14}H_{18}N_3Cl_1Se_1$ (342.73): C, 49.06; H, 5.29; N, 12.26. Found: C, 49.10; H, 5.33; N, 12.46. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-*tert*-Butylimino-3-methyl-5-tolyl-2,3-dihydro-6H-1,3,4-selenadiazine (4n). *Hydrobromide*: Yield: 2.50 g (62%), colorless rods (EtOH/Et_2O), mp 207 °C; IR (KBr, cm^{-1}): ν = 1030 (w), 1045 (w), 1080 (w), 1201 (s), 1245 (m), 1326 (s), 1380 (s), 1415 (s), 1495 (s), 1571 (s), 1620 (m), 2980 (s), 3190 (m). *Anal.*

Calcd for $C_{15}H_{22}N_3Br_1Se_1$ (403.23): C, 44.68; H, 5.50; N, 10.42. Found: C, 44.71; H, 5.46; N, 10.43. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless prisms (EtOH), mp 46 - 48 °C; IR (KBr, cm^{-1}): ν = 930 (s), 1015 (s), 1070 (m), 1120 (m), 1105 (s), 1330 (m), 1375 (s), 1421 (m), 1471 (m), 1615 (s), 2930 (s), 2990 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.37 (s, 9H, Me), 3.42 (s, 3H, N-Me), 3.66 (s, 2H, 6-CH_2, ^2J (SeH) = 16.9 Hz), 7.18 - 7.63 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): ν = 16.1 (C_6), 21.2, 29.6, 43.5, 53.8, 125.9, 129.1, 132.5, 139.2, 143 (C_2), 150.7, ^1J (Se, C_6), ^1J (Se, C_2) 150.2 Hz; ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 269.0. *Anal.* Calcd for $C_{15}H_{21}N_3Se$ (322.3): C, 55.90; H, 6.57; N, 13.04. Found: C, 55.87; H, 6.81; N, 12.84.

2-Isopropylimino-3-methyl-5,6-diphenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4o). *Hydrobromide*: Yield: 2.80 g (62%), colorless prisms (EtOH), mp 207 °C; IR (KBr, cm^{-1}): ν = 1140 (m), 1180 (m), 1225 (m), 1330 (s), 1380 (s), 1410 (s), 1445 (s), 1501 (s), 1580 (s), 2980 (s), 3075 (s), 3140 (s). *Anal.* Calcd for $C_{19}H_{22}N_3Br_1Se_1$ (451.28): C, 50.57; H, 4.91; N, 9.31. Fo und: C, 50.65; H, 4.82; N, 9.47. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, light yellow prisms (EtOH), mp 96 - 97 °C; IR (KBr, cm^{-1}): ν = 920 (m), 970 (m), 1020 (s), 1070 (s), 1135 (m), 1181 (s), 1215 (s), 1245 (s), 1270 (s), 1375 (m), 1390 (m), 1455 (s), 1501 (s), 1602 (s), 2980 (s); ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 0.97 - 1.05 (q, 6H, *i*Pr), 3.20 - 3.26 (m, 1H, CH), 3.54 (s, 3H, N-Me), 6.0 (s, 1H, CH, ^2J (SeH) = 28.3 Hz), 7.19 - 7.78 (m, 10H, ArH); ^{13}C NMR (DMSO-d_6, 75 Hz): δ = 24.51, 24.80, 33.80 (C_6), 38.66, 54.85, 125.66, 127.0, 127.45, 128.57, 128.83, 129.01, 135.82, 139.12, 142.65 (^1J (Se, C_6) = 55.2 Hz., ^1J (Se, C_2) = 138 Hz); ^{77}Se NMR (DMSO-d_6, Me_2Se): δ = 355.1; MS (EI, 70 eV): *m/z* = 371 (M^+, 18), 302 (4), 259 (3), 222 (87), 179 (100), 152 (3), 145 (8), 97 (3), 83 (3), 51 (2), 43 (2). *Anal.* Calcd for $C_{19}H_{21}N_3Se_1$ (370.36): C, 61.62; H, 5.72; N, 11.35. Found; C, 61.71; H, 5.61; N, 11.18.

2-Isopropylimino-3,6-dimethyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4p). *Hydrobromide*: Yield: 2.92 g (75%), colorless needles ($EtOH/Et_2O$), mp 200 - 202 °C; IR (KBr, cm^{-1}): ν = 1060 (m), 1145 (s), 1220 (s), 1330 (s), 1382 (s), 1405 (s), 1445 (s), 1480 (s), 1585 (s), 2990 (s), 3140 (m). *Anal.* Calcd for $C_{14}H_{20}N_3Br_1Se_1$ (389.21): C, 43.21; H, 5.18; N, 10.80: Found: C, 43.32; H, 5.21; N, 10.60. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, light yellow rods (EtOH), mp 84 - 86 °C; IR (KBr, cm^{-1}): ν = 910 (w), 990 (w), 1045 (m), 1130 (m), 1180 (m), 1225 (s), 1280 (s), 1350 (m), 1390 (m), 1460 (m), 1590 (s), 2930 (s), 2980 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.96 - 1.99 (d, 6H, *i*Pr), 2.36 (s, 3H, Me), 3.14 - 3.22 (q, 1H, CH), 3.68 (s, 2H, 6-CH_2), 7.16 - 7.64 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 15.17, 21.25, 24.44, 43.34, 58.23, 125.98, 129.26, 132.54, 139.47, 148.92, 149.49; MS: *m/*z = 309 (M^+, 8) 240 (16), 160 (18), 117 (100), 91 (8), 77 (6), 51 (3), 43 (4). *Anal.* Calcd for $C_{14}H_{19}N_3Se_1$

(308.29): C, 54.55; H, 6.21; N, 13.63. Found: C, 54.62; H, 6.34; N, 13.55.

2-Isopropylimino-3-methyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4q). *Hydrobromide*: Yield: 2.25 g (60%), colorless lamella (EtOH/Et_2O), mp 222 °C; IR (KBr, cm^{-1}): ν = 915 (s), 1030 (m), 1080 (s), 1155 (s), 1190 (m), 1252 (s), 1320 (s), 1380 (s), 1420 (s), 1461 (s), 1490 (s), 1581 (s), 2980 (s). *Anal.* Calcd for $C_{13}H_{18}N_3Br_1Se$ (375.18): C, 41.62; H, 4.84; N , 11.20. Found: C, 41.73; H, 4.92; N, 11.30. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless rods (EtOH), mp 82 - 83 °C; IR (KBr, cm^{-1}): ν = 920 (s), 1025 (s), 1071 (m), 1140 (m), 1180 (m), 1210 (s), 1240 (s), 1345 (s), 1420 (s), 1450 (s), 1602 (s), 2930 (s), 2980 (s); ^{1}H NMR $CDCl_3$, 300 MHz): δ= 1.18 (d, 6H, *i*Pr, *J* = 6.2 Hz), 3.14 - 3.22 (m, 1H, CH), 3.52 (s, 3H, N-Me): 3.73 (s, 2H, 6-CH_2, ^2J (SeH): 15.2 Hz), 7.36 - 7.75 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ= 14.7 (C_6), 24.5, 43.7, 58.2, 123.7, 127.6, 131.8, 134.5, 147.2 (C_2), 147.7 (^1J (Se, C_6) = 25.5 Hz, ^1J (Se, C_2) = 134 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se): δ= 241.0; MS (EI, 70 eV): *m/z* = 295 (M^+, 12), 226 (43), 183 (5), 145 (6), 117 (3), 103 (100), 83 (4), 77 (13), 51 (3), 43 (6). *Anal.* Calcd for $C_{13}H_{17}N_3Se_1$ (294.26): C, 53.06; H, 5.82; N, 14.28. Found: C, 53.07; H, 5.87; N, 14.40.

2-Isopropylimino-3-methyl-5-(4-bromophenyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4r). *Hydrobromide*: Yield: 4.86 g (63%), colorless needles (EtOH/Et_2O), mp 219 - 221 °C. *Anal.* Calcd for $C_{13}H_{17}N_3Br_2Se_1$ (454.08): C, 34.39; H, 3.77; N, 9.25. Found: C, 34.87; H, 3.81; H, 9.24. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless solid (EtOH), mp 73 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (d, 6H, *i*Pr, *J* = 6.2 Hz), 3.15 - 3.23 (m, 1H, CH), 3.53 (s, 3H, N-Me), 3.66 (s, 2H, 6-CH_2, ^2J (SeH) = 16.2 Hz), 7.50 - 7.61 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.7 (C_6), 24.5, 43.6, 58.1, 123.6, 127.6, 131.7, 134.5, 147.14, 147.7 (^1J (Se, C_6) = 52.6 Hz, ^1J (Se, C_2) = 133 Hz); ^{77}Se NMR ($CDCl_3$), Me_2Se): δ = 238.0. *Anal.* Calcd for $C_{13}H_{16}N_3Br_1Se_1$ (373.16): C, 41.84; H, 4.32; N, 11.26. Found: C, 41.89; H, 3.35; N, 11.28.

2-Isopropylimino-3-methyl-5-(4-chlorophenyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4s). *Hydrobromide*: Yield: 3.76 g (92%), colorless needles (EtOH/Et_2O), mp 220 °C. *Anal.* Calcd for $C_{13}H_{17}N_3Br_1Cl_1Se_1$ (409.62): C, 38.12; H, 4.18; N, 10.26. Found: C, 38.24; H, 4.20; N, 10.32. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless needles (EtOH/H_2O), mp 69 - 71 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.15 (d, 6H, *i*Pr), 3.16 (m, 1H, C*H*-*i*Pr), 3.47 (s, 3H, N-Me), 3.61 (s, 2H, 6-CH_2), 7.49 - 7.55 (m, 4H, ArH); MS (EI, 70 eV): *m/z* = 329 (M^+, 8), 260 (53), 137 (100), 101 (13), 83 (6), 57 (3), 43 (13). *Anal.* Calcd for $C_{13}H_{16}N_3Cl_1Se_1$ (328.71): C, 47.50; H, 4.91; N, 12.78: Found: C, 47.62; H, 4.82; N, 12.54. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Isopropylimino-3-methyl-5-tolyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4t). *Hydrobromide*: Yield: 2.41 g (62%), colorless rods (EtOH/ Et_2O), mp 206 - 208 °C. *Anal.* Calcd for $C_{14}H_{20}N_3Br_1Se_1$ (389.21): C, 43.21; H, 5.18; N, 10.80. Found: C, 43.25; H, 5.21; N, 10.82. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, colorless rods (EtOH), mp 47 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.17 (d, 6H, *i*Pr), 2.34 (s, 3H, 4-Me), 3.14 (m, 1H, C*H*-*i*Pr), 3.49 (s, 3H, N-Me), 3.65 (s, 2H, 6-CH_2), 7.36 (m, 4H, ArH). *Anal.* Calcd for $C_{14}H_{19}N_3Se_1$ (308.29): C, 54.55; H, 6.21; N, 13.63. Found: 54.63; H, 6.36; N, 13.59. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Isopropylimino-3-methyl-5-(4-fluorophenyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4u). *Hydrobromide*: Yield: 3.37 g (95%), colorless prisms (EtOH/Et_2O), mp 218 °C; MS (EI, 70 eV): *m/z* = 313 (10), 244 (44), 201 (6), 163 (3), 135 (3), 121 (100), 101 (8), 80 (6), 43 (6). *Anal.* Calcd for $C_{19}H_{17}N_3Br_1F_1Se_1$ (393.17): C, 39.71; H, 4.36; N, 10.69. Found: C, 39.54; H, 4.38; N, 10.53. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, light yellow solid (EtOH), mp 75 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 1.19 (d, 6H, *i*Pr), 3.21 (m, 1H, C*H*-*i*Pr), 3.57 (s, 3H, N-Me), 3.70 (s, 2H, 6-CH_2), 7.41 - 7.52 (m, 4H, ArH); MS (EI, 70 eV): *m/z* = 312 (M^+, 6), 244 (32), 201 (6), 163 (5), 135 (3), 121 (100), 101 (19), 76 (7), 43 (17), 41 (10), 28 (4). *Anal.* Calcd for $C_{19}H_{16}N_3F_1Se_1$ (312.25): C, 50.01; H, 5.16; N, 13.46. Found: C, 50.31; H, 5.40; N, 13.41. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-(*n*-Propyl)imino-3-methyl-5,6-diphenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4v). *Hydrobromide*: Yield: 2.75 g (61%), colorless prisms (EtOH/Et_2O), mp 190 - 192 °C; IR (KBr, cm^{-1}): ν = 930 (m), 1090 (m), 1184 (m), 1220 (m), 1375 (s), 1471 (s), 1595 (s), 2980 (s). *Anal.* Calcd for $C_{19}H_{22}N_3Br_1Se_1$ (451.28): C, 50.57; H, 4.91; N, 9.31. Found: C, 50.63; H, 4.87; N, 9.47. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100% of yellow prisms (EtOH), mp 75.5 - 76 °C; ^{1}H NMR (DMSO-d_6, 300 MHz: δ = 0.83 (t, 3H, Me), 1.40 - 1.50 (m, 1H, C*H*-Pr), 2.97-3.04 (m, 1H, N-CH_2-Pr), 3.56 (s, 3H, N-Me), 6.00 (s, 1H, 6-CH, ^2J (SeH) = 28.3 Hz), 7.20 - 7.74 (m, 10H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 11.70, 24.35, 33.85, (C_6), 55.47, 125.66, 127.01, 127.47, 128.58, 128.82, 129.04, 135.79, 139.07, 142.65, 145.09, ^1J (SeC_2) = 140 Hz; ^{77}Se NMR (DMSO-d_6, Me_2Se): δ = 358.0. *Anal.* Calcd for $C_{19}H_{21}N_3Se_1$ (370.36): C, 61.62; H, 5.72; N, 11.35. Found: C, 61.65; H, 5.75; N, 11.18.

2-Propylimino-3,6-dimethyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4w). Yield: 2.79 g (70%), colorless solid (EtOH), mp 186 °C; IR (KBr, cm^{-1}): ν = 990 (w), 1091 (w), 1145 (w), 1225 (m), 1280 (w), 1365 (s), 1467 (s), 1591 (s), 2990 (s), 3080 (s); ^{1}H NMR (DMSO-d_6, 100 MHz): δ = 1.00 (t, 3H, Me-*n*Pr), 1.70 (d, 3H, 6-Me), 1.75 (d, 2H, CH_2), 3.50 (s, 2H, N-CH_2), 3.85 (s, 3H, N-Me), 4.98 (q, 1H, 6-CH), 7.51 -

7.76 (m, 5H, ArH). *Anal.* Calcd for $C_{14}H_{20}N_3Br_1Se_1$ (389.21): C, 43.21; H, 5.18; N, 10.80. Found: C, 42.91; H, 5.20; N, 10.60. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Propylimino-3-methyl-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4x). *Hydro-bromide*: Yield: 3.45 g (92%), colorless rods (EtOH), mp 219 - 220 °C; IR (KBr, cm^{-1}): ν = 930 (m), 1090 (m), 1135 (m), 1190 (m), 1220 (m), 1250 (w), 1325 (s), 1371 (s), 1435 (s), 1461 (s), 1595 (s), 2910 (s), 2980 (s), 3035 (s), 3100 (s). *Anal.* Calcd for $C_{13}H_{18}N_3Br_1Se_1$ (375.18): C, 41.62; H, 4.84; N, 11.20. Found: C, 41.71; H, 4.81; N, 11.31. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 95%, yellow rods, mp 77 - 79 °C; ^1H NMR ($CDCl_3$, 100 MHz): δ = 0.99 (t, 3H, N-CH_2), 1.75 (m, 2H, CH_2-nPr), 3.59 (t, 2H, N-CH_2), 3.77 (s, 3H, N-Me), 4.15 (s, 2H, 6-CH_2), 7.50 - 7.72 (m, 5H, ArH). *Anal.* Calcd for $C_{13}H_{17}N_3Se_1$ (294.26): C, 53.06; H, 5.82; N, 14.20; Se, 26.83. Found: C, 53.12; H, 5.82; N, 14.40; Se, 26.79. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

2-Imino-3-methyl-5-(4-chlorphenyl)-2,3-dihydro-6*H*-1,3,4-selenadiazine (4y). *Hydrochloride*: Yield: 3.10 g (96%), colorless rods (EtOH), mp 250 - 251 °C; MS (EI, 70 eV): *m/z* = 287 (M^+, 20), 285 (12), 260 (7), 180 (27), 137 (100), 127 (25), 102 (22), 75 (1), 43 (8). *Anal.* Calcd for $C_{10}H_{11}N_3Cl_2Se_1$ (323.08): C, 37.18; H, 3.44; N, 13.01. Found: C, 37.20; H, 3.51; N, 13.20. Due to the low solubility, NMR spectra could not be obtained. *Free base*: Yield: 100%, yellow needles (EtOH), mp 93 - 93.5 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.62 (s, 3H, N-Me), 3.78 (s, 2H, 6-CH_2, ^2J (SeH): 14.6 Hz), 7.12 (s, 1H, NH), 7.36 - 7.69 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.4 (C_6), 41.6, 127.4, 128.8, 133.8, 135.6, 145.7, 153.3 (C_2, ^1J (Se, C_6) = 53.5 Hz, ^1J (Se, C_2) = 138 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se): δ = 277.0; MS (EI, 70 eV): *m/z* = 287 (M^+, 20), 285 (12), 260 (7), 180 (27), 137 (100), 127 (25), 102 (22), 75 (12), 48 (8). *Anal.* Calcd for $C_{10}H_{10}N_3Cl_1Se_1$ (286.62): C, 41.91; H; 3.52; N, 14.66. Found: C, 41.82; H, 3.61; N, 14.72.

2-(*sec*-Butyl)imino-3-methyl-5,6-diphenyl-6*H*-1,3,4-selenadiazine (4z). *Hydrobromide*: Yield: 2.70 g (58%), colorless solid, mp 124 - 125 °C; ^1H NMR (DMSO-d_6, 300 MHz): δ= 0.41-1.75 (m, 8H, *s*Bu), 3.76 (s, 1H, CH), 3.84 (s, 3H, N-Me), 6.64 (s, 1H, 6-CH, ^2J (SeH): 27.1 Hz), 7.06 - 7.92 (m, 10H, ArH), 9.37 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 10.49, 19.73, 20.79, 28.73, 58.76, 126.8, 127.28, 128.31, 128.69, 129.07, 129.24, 130.27, 131.80, 132.70, 134.94, 153.53; ^{77}Se NMR (DMSO-d_6, Me_2Se): δ = 421.0. *Anal.* Calcd for $C_{20}H_{24}N_3Br_1Se_1$ (465.30): C, 51.63; H, 5.20; N, 9.03. Found: C, 51.82; H, 5.25; N, 9.08.

2-Phenylimino-3,5-dimethyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4aa). *Hydrobromide:* Starting with 2-methyl-4-phenyl-thiosemicarbazide (1.78 g, 10.0 mmol), bromoacetone (1.37 g, 10.0 mmol, dissolved in

5 mL of EtOH) in 10 mL of EtOH, **4aa** was isolated as a yellow prisms (from EtOH, 2.45 g, 71%), mp 188 - 189 °C; ^{1}H NMR (CD_3OD, 300 MHz): δ = 2.31 (s, 3H, Me), 3.61 (s, 2H, 6-CH_2), 3.80 (s, 3H, NMe), 6.91 - 7.62 (m, 5H, ArH). *Anal.* Calcd for $C_{11}H_{14}N_3Br_1Se_1$ (347.1): C, 38.73; H, 4.14; N, 12.32. Found: C, 38.56; H, 4.20; N, 12.34.

2-(*tert*-Butyl)imino-3-(2-hydroxyethyl)-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine (4ab). *Hydrobromide*: To an ethanol solution (15 mL) of 4-(*tert*-butyl)-2-hydroxyethylselenosemicarbazide (2.38 g, 10.0 mmol) was dropwise added (1.99 g, 10.0 mmol) an ethanol solution (10 mL) of phenacyl bromide at 0 °C. The solution was stirred for 30 min at 20 °C and for 3 min under reflux. The hot solution was filtered and the filtrate was cooled to 0 °C to give a precipitate of colorless crystals (2.64 g, 63%), mp 185 - 186 °C. *Anal.* Calcd for $C_{15}H_{22}N_3BrOSe$ (419.22): C, 42.97; H, 5.28; N, 10.02. Found: C, 42.91, H, 3.22; N, 10.21. *Hydrochloride*: The hydrobromide was dissolved in ethanol and ammonia was added. The free base separated as an oil. The oil was separated, washed with water and dissolved in a solution of HCl in ethanol. Addition of Et_2O resulted in precipitation of the hydrochloride.

2-Imino-3-(2-hydroxyethyl)-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine hydrochloride (4ac). The hydrochloride of 2-(*tert*-butyl)imino-3-(2-hydroxyethyl)-5-phenyl-2,3-dihydro-6*H*-1,3,4-selenadiazine **4ab** (0.948 g, 2.5 mmol) was dissolved in conc. hydrochloric acid (5 mL) and the solution was refluxed for 30 min. Colorless crystals formed which were filtered off and recrystallized from EtOH (0.69 g, 87%), mp 225 - 226 °C. *Anal.* Calcd for $C_{11}H_{14}N_3ClOSe$ (318.66): C, 41.46; H, 4.43; N, 13.18. Found: C, 41.51, H, 4.52; N, 12.91. Due to low solubility, NMR spectra could not be obtained.

3-Phenylamino-4,5-diphenylpyrazole (5a). 4.71 g (10 mmol) **2a·HBr** was refluxed in acetic acid (20 mL) for 2 h. The hot solution was filtered. To the solution was added a dilituted aqueous solution of ammonia until pH = 8 was reached. A precipitate formed which was filtered off and recrystallized from benzene/petroleum ether. Yield: 2.9 g (93%), colorless needles, mp 181 - 183 °C; IR (KBr, cm^{-1}): ν = 696 (s), 749 (s), 769 (m), 1016 (w), 1240 (m), 1312 (m), 1442 (m), 1463 (m), 1497 (s), 1537 (s), 1572 (m), 1602 (s), 3031 (m), 3056 (m), 3189 (m), 3426 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.88 (s, br, 1H, NH), 6.87 (s, br, 1H, NH) 7.30 - 7.42 (m, 15H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 114.47, 117.68, 126.32, 127.31, 127.81, 128.35, 128.48, 129.59, 132.50; MS (EI, 70 eV): *m/z* = 311 (M^+, 100), 218 (5), 207 (2), 178 (4), 155 (2), 104 (3), 77 (7), 28 (16). *Anal.* Calcd for $C_{21}H_{17}N_3$ (311.38): C, 81.00; H, 5.50; N, 13.49. Found: C, 81.04; H, 5.53; N 13.51.

3-Phenylamino-4-methyl-5-diphenylpyrazole (5b). 1.64 g (5 mmol) of **2b** was refluxed in acetic acid (25 mL) for 3 h. The hot solution was filtered. To the solution was added a dilituted aqueous solution of ammonia until pH = 8 was reached. Yield: 0.87 g (70%), colorless needles (benzene/petroleum ether), mp 137 - 139 °C; MS (EI, 70 eV): *m/z* = 252 (M^+, 10), 249 (100), 220 (3), 206 (3), 172 (3), 157 (6), 145 (25), 130 (4), 115 (8), 93 (8), 77 (9), 65 (2), 51 (2); ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 2.08 (s, 3H, Me), 6.8 - 7.55 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 8.37, 104.08, 115.22, 119.46, 127.06, 128.16, 128.88, 129.1, 130.67, 141.75, 144.04, 149.64. *Anal.* Calcd for $C_{16}H_{15}N_3$ (249.3) C, 77.08; H, 6.06; N,16.85. Found: C, 77.02; H, 6.09; N, 16.76.

3-*tert*-Butylamino-4,5-diphenylpyrazole (5c). 185 mg (0.5 mmol) of **2g** was refluxed in acetic acid (5 mL) for 1 h. Yield: 80 mg (55%), colorless needles (EtOH/H_2O), mp 211 - 212 °C; IR (KBr): ν = 609 (m), 698 (s), 734 (m), 762 (m), 1019 (m), 1210 (m), 1229 (m), 1284 (m), 1362 (m), 1389 (m), 1444 (m), 1462 (m), 1482 (m), 1514 8s), 1589 (m), 1602 (s), 2976 (s), 3057 (m), 3240 (s) cm^{-1}; MS (EI, 70 eV): *m/z* = 291 (M^+, 40), 276 (100), 235 (39), 206 (3), 178 (6,5), 165 (4), 131 (2), 104 (3,5), 89 (2), 77 (3), 41 (3). *Anal.* Calcd for $C_{19}H_{21}N_3$ (291.40): C, 78.32; H, 7.26; N, 14.42. Found: C, 78.41; H, 7.32; N, 14.48.

3-*tert*-Butylamino-4-methyl-5-phenylpyrazole (5d). 154 mg (0.5 mmol) of **2h** was refluxed in acetic acid (5 mL) for 4 h. Yield: 90 mg (79%), colorless prisms (*n*-hexane), mp 84 - 85 °C; IR (KBr): ν = 691 (s), 770 (m), 995 (m), 1195 (m), 1229 (m), 1247 (m), 1340 (m), 1374 (m), 1400 (m), 1415 (s), 1447 (s), 1487 (s), 1556 (s), 1594 (m), 1974 (s), 3062 (m), 3165 (m) cm^{-1}; MS (EI, 70 eV): *m/z* = 229 (M^+, 42), 214 (100), 173 (58), 157 (3), 144 (2), 130 (4), 115 (8), 96 (5), 77 (6), 70 (7), 57 (4); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.36 (s, 9H, *t*Bu), 2.02 (s, 3H, Me) 7.30 - 7.51 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 8.26, 29.85, 52.27, 101.68, 127.15, 127.81, 128.73, 131.58, 141.72, 152.9. *Anal.* Calcd for $C_{14}H_{19}N_3$ (229.33): C, 73.33; H, 8.35; N,18.32. Found: C, 73.28; H, 8.39; N,18.36.

3-*n*-Propylamino-4,5-diphenylpyrazole (5e). 218 mg (0.5 mmol) of **2o· HBr** was refluxed in acetic acid (5 mL) for 3 h. The hot solution was filtered. To the solution was added a dilituted aqueous solution of ammonia until pH = 8 was reached. Yield: 100 mg (73%); IR (KBr): ν = 696 (s), 734 (m), 769 (s), 963 (m), 1159 (m), 1442 (s), 1480 (s), 1530 (s), 1573 (m), 1603 (s), 2873 (s), 3057 (m), 3104 (m), 3200 (m), cm^{-1}; MS (EI, 70 eV): *m/z* 277 (M^+ 90), 248 (100), 234 (21), 219 (5), 178 (4), 165 (4), 123 (2), 104 (3), 77 (2), 43 (2); ^{1}H NMR ($(CD_3)_2CO$, 200 MHz), δ = 0.84 - 0.93 (t, 3H, Me), 1.55 - 1.75 (m, 2H, CH_2), 3.18 - 3.28 (t, 3H, NMe), 7.19 - 7.45 (m, 10H, ArH); ^{13}C NMR ($(CD_3)_2CO$, 50 MHz) δ = 11.82, 23.68, 46.72, 126.82, 128.2, 128.44, 129.18, 129.45, 130.44, 134.67, 206.16. *Anal.* Calcd for $C_{18}H_{19}N_3$ (277.37): C, 77.95; H,

6.90; N, 15.15. Found: C, 77.82; H, 6.86; N, 15.17.

3-*n*-Propylaminoamino-4-methyl-5-phenylpyrazole (5f). *Hydrochloride:* 294 mg (1 mmol) of **2p** was refluxed in acetic acid (5 mL) for 24 h. The hot solution was filtered. The solvent was removed in vacuo and to the residue was added Et_2O. Hydrogen chloride gas was added to give a yellow precipitate (180 mg, 72%). Colourless plates (EtOH/Et_2O), mp 195 -196 °C. *Anal.* Calcd for $C_{13}H_{18}N_3Cl$ (251,3): C, 62.13; H, 6.82; N, 16.72. Found: C, 62.18; H, 6.89; N, 16.76.

2-Isopropylamino-4,5-diphenylpyrazole (5g). 437 mg (1 mmol) of **2k·HBr** was refluxed in acetic acid (5 mL) for 3 h. The hot solution was filtered. To the solution was added a dilituted aqueous solution of ammonia until pH = 8 was reached. Yield: 190 mg (69%), colorless needles, mp 178 - 180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.21 - 1.25 (d, 6H, *i*Pr), 3.79 - 3.87 (m, 1H, CH), 7.30 - 7.39 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 23.54, 45.42, 105.42, 126.51, 127.39, 128.22, 128.66, 128.91, 129.72, 130.35, 132.85, 141.20, 154.19. *Anal.* Calcd for $C_{18}H_{19}N_3$ (277.37): C, 77.95; H, 6.90; N, 15.15. Found: C, 77.83; H, 6.86; N, 15.18.

3-Isopropylaminoamino-4-methyl-5-phenylpyrazole (5h). *Hydrochloride:* 147 mg (5 mmol) **2l** was refluxed in acetic acid (5 mL) for 24 h. The hot solution was filtered. The solvent was removed in vacuo and to the residue was added Et_2O. Hydrogen chloride gas was added to give a yellow precipitate. Yield: 70 mg (56%), colorless needles (EtOH/Et_2O), mp 217 -219 °C. *Anal.* Calcd for $C_{13}H_{18}N_3Cl$ (251.3): C, 62.13; H, 6.82; N,16.72. Found: C, 62.19; H, 6.79; N,16.66.

1-Methyl-3-phenyl-5-phenylaminopyrazole (5i). Compound **4c** (820 mg, 2.5 mmol) was refluxed in glacial acetic acid (5 mL) for 24 h. After cooling, the solution was filtered and concentrated under reduced pressure. The solid obtained was recrystallized from EtOH/H_2O. Yield: 460 mg (74%), colorless prisms (EtOH/H_2O), mp 151.5 - 152.5 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 3.71 (s, 3H, NMe), 5.37 (s, 1H, NH,), 6.33 (s, 1H CH), 7.11 (m, 10H, ArH). *Anal.* Calcd for $C_{16}H_{15}N_3$ (249.32): C, 77.08; H, 6.06; N, 16.85. Found: C, 77.21; H, 5.88; N, 16.82. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

1,3-Dimethyl-4-phenyl-5-phenylaminopyrazole (5j). Compound **4g** (342 mg, 1.0 mmol) in glacial acetic acid (5 mL) was refluxed for 5 h. After cooling, the solution was filtered and concentrated under reduced pressure. The solid obtained was recrystallized from EtOH/H_2O. Yield: 210 mg (80%), colorless prisms (EtOH/H_2O), mp 148 - 150 °C; ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 2.34 (s, 3H, CMe), 3.65 (s, 3H, NMe),

5.39 (s, 1H, NH), 7.11 (m, 10H, ArH). *Anal.* Calcd for $C_{17}H_{17}N_3$ (263.34): C, 77.54; H, 6.51; N, 15.96. Found: C, 77.51; H, 6.58; N, 15.82. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

1,3,4-Trimethyl-5-phenylaminopyrazole (5k). Compound **4h** (560 mg, 2.0 mmol) in glacial acetic acid (5 mL) was refluxed for 10 h. After cooling, the solution was filtered and concentrated under reduced pressure. The solid obtained was recrystallized from EtOH/H_2O. Yield: 320 mg (80%), colorless prisms (EtOH/H_2O), mp 137 - 139 °C; ^1H NMR ($CDCl_3$, 100 MHz): δ = 1.80 (s, 3H, C_4-Me), 2.17 (s, 3H, C_3-Me), 3.60 (s, 3H, NMe), 5.22 (s, 1H, NH), 6.79 (m, 5H, ArH). *Anal.* Calcd for $C_{16}H_{15}N_3$ (201.27): C, 71.61; H, 7.51; N, 20.88. Found: C, 71.61; H, 7.58; N, 20.82. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

1-Methyl-3,4-diphenyl-5-(*tert*-butyl)aminopyrazole (5l). Compound **4i** (384 mg, 1.0 mmol) in glacial acetic acid (5 mL) was refluxed for 30 min. After cooling, the solution was filtered and concentrated under reduced pressure. The solid obtained was recrystallized from EtOH/H_2O. Yield: 290 mg (95%), colorless prisms (*n*-hexane), mp 112 -113 °C; ^1H NMR ($CDCl_3$, 100 MHz): δ = 0.90 (s, 9H, *t*Bu), 3.14 (s, 1H, NH), 3.86 (s, 3H, NMe), 7.30 (m, 5H, ArH). *Anal.* Calcd for $C_{20}H_{23}N_3$ (305.42): C, 78.65; H, 7.59; N, 13.76. Found: C, 78,41; H, 7.58; N, 13.72. Due to the low solubility, a ^{13}C NMR spectrum could not be obtained.

1,2-Dimethyl-3-phenyl-5-*tert*-butyliminopyrazoline hydrobromide (7a). Phenacyl bromide (1.99 g, 10 mmol) was dissolved in EtOH (30 mL). This solution was added dropwise in 30 min under cooling with ice to 1,2-dimethyl-4-*tert*-butyl-selenosemicarbazide **6** (2.22 g, 10 mmol) in EtOH (10 mL). A precipitate of red selenium formed. The solution was stirred for 30 min at 20 °C. The mixture was allowed to stand 24 h and subsequently was refluxed in the water bath at 70 °C for 5 min. The selenium was filtered off. The solvent was evaporated under reduced pressure to give a yellow oil which was dissolved in dry EtOH. The ethanolic solution was added dropwise to 150 mL of Et_2O. A light yellow precipitate formed. Yield 1.75 g (54%), light beige prisms (EtOH/Et_2O), mp 155 - 156 °C; IR (KBr, cm^{-1}) ν = 7058 (m), 795 (m), 835 (m), 945 (m), 1212 (m), 1391 (m), 1402 (m), 1465 (m), 1608 (s), 2981 (s), 3210 (m); ^1H NMR (CD_3OD, 100 MHz): δ = 1.45 (s, 9H, *t*Bu-Me), 3.78 (s, 3H, NMe), 3.86 (s, 3H, NMe), 5.28 (s, 1H, 4-H-Hetar), 7.32 - 7.92 (m, 5H, ArH). *Anal.* Calcd for $C_{15}H_{22}N_3Br$ (324.26): C, 55.56; H, 6.84; N, 12.96. Found: C 55.60, H 6.85, N 12.91.

1,2-Dimethyl-3-(4-chlorophenyl)-5-*tert*-butyliminopyrazoline hydrobromide (7b). This compound was obtained by reaction of **6** (2.22 g, 10 mmol) with 4-chloro-phenacyl bromide (2.36 g, 10 mmol) as described for **7a**. Yield: 2.2 g (62%), colorless prisms (EtOH/Et_2O), mp 200 - 202 °C; IR (KBr, cm^{-1}) ν = 701 (m), 765

(m), 845 (w), 990 (m), 1130 (m), 1297 (1300 (m), 1486 (s), 1531 (m), 1615 (s), 2990 (m); ^{1}H NMR (CD_3OD, 100 MHz): δ = 1.51 (s, 9H, *t*Bu-Me), 3.88 (s, 3H, NMe), 4.31 (s, 3H, N-Me), 5.92 (s, 1H, 4-H-Hetar), 7.33 - 7.83 (m, 4H, ArH). *Anal.* Calcd for $C_{15}H_{21}N_3ClBr$ (358.71): C, 50.23; H, 5.90; N, 11.71. Found: C, 50.30; H, 5.91; N, 11.82.

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