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Facile Synthesis and Structure of Novel 2,5-Disubstituted 1,3,4-Selenadiazoles

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The reaction of hydrazide with carbonyl chloride in the presence of sodium carbonates leads to the corresponding 1,2-diacylhydrazines [**1a**–**t**, $R^1C(O)NHNHC(O)R^2$, R^1 = aryl, R^2 = aryl or alkyl] in moderate to excellent yield (57–90 %). The latter reacts with 2,4-diphenyl-1,3-diselenadiphosphetane-2,4-diselenide (Woollins' reagent, **WR**) in refluxing toluene to give a series of new 2,5-disubstituted 1,3,4-selenadiazoles (**2a**–**t**, 51–99 % yield). All compounds were characterized spectroscopically and six compounds were characterized crystallographically.

Introduction

The synthesis of the organoselenium compound diethyl selenide was first reported in 1836.[1] It was not until the 1970s, where the use of diethyl selenide in several new reactions created a variety of novel structures with unusual properties, that these compounds began to attract more general interest. The interest in using organoselenium heterocycles as potential pharmaceuticals and new materials, as well as reagents and catalysts expanded rapidly during last three decades.[2] For example, 1,3,4-selenadiazoles have been studied because of their potential activities as antibacterial, analgesic, antitumor, anticonvulsant, and antiinflammatory drugs, pesticides and fungicides.[3] Furthermore, some of them have been used as thermotropic liquid crystals, corrosion and oxidation inhibitors, or as dyes or metal ion complexation reagents.[4] However, little is known about the 2,5-disubstituted 1,3,4-selenadiazoles.[5] Several methods have been reported for their preparation, which include a ring-closure reaction of selenobenzamides with hydrazine hydrate,[6] reacting dimethylformamide azine with hydrogen selenide,[7] treatment of 1,2-diacetylhydrazine with phosphorus pentaselenide,[8] reaction of isoselenocyanates with selenosemicarbazides[9] or a carboxylic acid with selenosemicarbazide and phosphoryl chloride.[10] However, the examples of these compounds in the literature are limited due to either lack of starting materials or very low yield.

2,4-Diphenyl-1,3-diselenadiphosphetane 2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$, known as Woollins' reagent (**WR**), is the selenium counterpart of the well-known Lawesson's reagent $[p\text{-}MeOC_6H_4P(S)(\mu\text{-}S)]_2$ (**LR**). **LR** has been used extensively for various thionation reactions.[11] Compared with other selenation reagents **WR** has broad utility and is useful in the synthesis of a wide range of selenium-containing compounds. These compounds include large P/Se molecular aggregates or metal complexes by nucleophilic ring-opening reactions with alkali-metal thiolates,[12] selenoamides and selenoaldehydes by simple oxygen/selenium exchange or reaction with ArCN followed by hydrolysis and a wide variety of P–Se heterocycles.[13] Here, we report the synthesis and characterization of a series of novel 2,5-disubstituted 1,3,4-selenadiazoles from the selenation of the corresponding 1,2-diacylhydrazine with **WR**. To the best of our knowledge, this is the first report of the systematic synthesis of 2,5-disubstituted 1,3,4-selenadiazoles. Furthermore, six examples, representing the first examples of this class have been structurally characterised.

Results and Discussion

Preparation of 1,2-diacylhydrazines **1a**–**t** was very straightforward using a modification of a literature method.[14] Reaction between hydrazides and carbonyl chlorides in the presence of sodium carbonate leads to the corresponding **1a**–**t** in good to excellent yields (57–90 %, Scheme 1 and Table 1). Even though most of the 1,2-diacylhydrazines had been previously synthesized; our modification of the literature preparation improved the yield and synthetic efficiency of their preparation. 1,2-Diacylhydrazines, **1a**–**t**, were characterised by IR, ^1H NMR, ^{13}C NMR and MS data. The Infrared spectrum of these compounds show a strong absorption in the region of 1599–1637 cm^{-1} and the ^{13}C NMR spectra display a characteristic peak in the region of 139.0–171.1 ppm, both are assignable to characteristic carbonyl groups, confirming the formation of 1,2-diacylhydrazines. There is also a characteristic ^1H NMR

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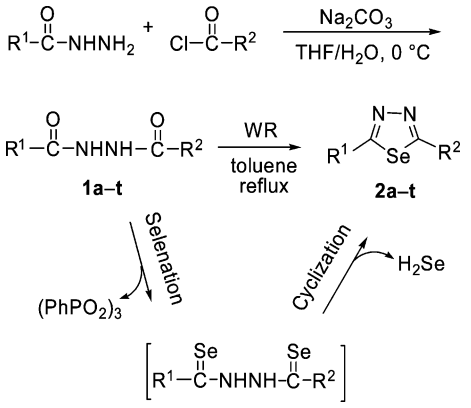
resonance from the NHNH group in the region of 9.80–10.69 ppm. Finally, the compounds display clear molecular ion peaks in their mass spectra.



Scheme 1. Synthesis of 1,2-diacylhydrazines **1a**–**t** and 2,5-disubstituted 1,3,4-selenadiazoles **2a**–**t**.

Table 1. Synthesis of 1,2-diacylhydrazines **1a**–**t** and 2,5-disubstituted 1,3,4-selenadiazoles **2a**–**t**.

R^1	R^2	**1**	Yield (%)	**2**	Yield (%)
C_6H_5	C_6H_5	**1a**	61	**2a**	98
4-BrC_6H_4	4-BrC_6H_4	**1b**	65	**2b**	75
C_6H_5	pyridin-3-yl	**1c**	77	**2c**	51
4-$MeOC_6H_4$	pyridin-3-yl	**1d**	82	**2d**	58
C_6H_5	4-MeC_6H_4	**1e**	63	**2e**	90
C_6H_5	4-ClC_6H_4	**1f**	67	**2f**	97
C_6H_5	4-BrC_6H_4	**1g**	69	**2g**	95
C_6H_5	4-FC_6H_4	**1h**	81	**2h**	91
C_6H_5	thiophen-2-yl	**1i**	70	**2i**	97
C_6H_5	C_2H_5O	**1j**	90	**2j**	99
C_6H_5	furan-2-yl	**1k**	81	**2k**	82
4-MeC_6H_4	furan-2-yl	**1l**	65	**2l**	90
4-BrC_6H_4	furan-2-yl	**1m**	63	**2m**	96
4-$MeOC_6H_4$	4-MeC_6H_4	**1n**	69	**2n**	90
4-$MeOC_6H_4$	C_6H_5	**1p**	77	**2p**	86
4-MeC_6H_4	4-ClC_6H_4	**1r**	68	**2r**	83
4-MeC_6H_4	4-FC_6H_4	**1s**	57	**2s**	79
4-MeC_6H_4	4-BrC_6H_4	**1t**	81	**2t**	75

2,5-Disubstituted 1,3,4-thiadiazoles, the sulfur counterpart of 2,5-disubstituted 1,3,4-selenadiazoles, have been examined as potential antibacterial,[15] antiviral,[16] analgesic,[17] antitumor,[18] anticonvulsant,[15] and antiinflammatory drugs, along with activity as pesticides and fungicides,[17,19] as well as other applications.[4a–4c,20] The most popular method for the synthesis of this class of compounds involves the cyclization and dehydration of thiohydrazides or other substrates with an S–C–N–N–C–S moiety.[4a,15,16] This is typically done via thionation of 1,2-diacylhydrazines with Lawesson's reagent, followed by spontaneous cyclization and dehydrosulfurization.[14c] Herein, we adopted a similar approach, that is, reacting 1,2-diacylhydrazines, **1a**–**t**, with **WR** to afford a series of 2,5-disubstituted 1,3,4-selenadiazoles, **2a**–**t**, in moderate to excellent yield (51–99%, Scheme 1 and Table 1). It should be noted in particular that reaction of **WR** with 1,2-diacylhydrazines bearing diaryl groups (R^1, R^2 = Aryl) is very fast and high yield (75–99%), while with the 1,2-diacylhydrazines bearing one aryl group and one pyridine group (R^1 = Aryl; R^2 = Pyr) is slow with relatively low yield (51 and 58% for compounds **2b** and **2c**, respectively), This is most likely due to the presence of the electron-withdrawing pyridine group. **2** are stable in air and moisture for several months and are soluble in common organic solvents.

The characterisation of **2a**–**t** is based on elemental analyses, ^1H, ^{13}C and ^{77}Se NMR, IR spectroscopy and mass spectrometry. The elemental analyses for all of these new compounds were satisfactory. All of compounds showed the anticipated molecular ion peaks $[M]^+$, $[M - H]^+$, $[M + H]^+$ or $[M + Na]^+$ in their mass spectra. The ν(C=N) vibrations are observed in the range of 1418–1495 cm^{-1}, comparable with related hetercycles.[21] The absence of ν (1599–1637 cm^{-1} for C=O) and the presence of the typical ^{13}C NMR signals in the range of 133.1–174.9 ppm for C=N double bond and ^{77}Se NMR signals in the range of 683.01–714.61 ppm indicate the formation of the five-membered ring systems, **2a**–**t**.

Surprisingly, to date, there have been no crystal structures of 1,3,4-selenadiazole yet reported. Here we report the structures of six examples **2b**, **2h**, **2k**, **2m**, **2p** and **2s** (Figure 1). Colourless block crystals of these compounds were obtained for X-ray analysis via slow evaporation of a dichloromethane solution into hexane. Details of the selected interatomic distances and angles are given in Table 2. Unfortunately, the data for **2g** could not be well-refined though the structure is closely similar to the other six described here.[22] The overall molecular structures of these compounds are very similar in geometry. The C_2N_2Se rings are approxi-

Table 2. Selected interatomic distances (Å) and angles (°) for **2b**, **2h**, **2k**, **2m**, **2p** and **2s**.

	2b	**2h**	**2k**	**2m**	**2p**	**2s**
Se(1)–C(1)	1.885(10)	1.891(7)	1.861(5)	1.869(9)	1.880(3)	1.902(5)
Se(1)–C(2)	1.884(10)	1.884(7)	1.887(5)	1.894(8)	1.877(3)	1.890(5)
C(2)–N(2)	1.295(13)	1.296(9)	1.302(7)	1.299(12)	1.298(4)	1.301(6)
N(2)–N(1)	1.381(12)	1.363(8)	1.374(7)	1.380(10)	1.373(4)	1.379(6)
C(1)–N(1)	1.276(12)	1.307(9)	1.302(7)	1.295(12)	1.297(4)	1.294(6)
C(1)–Se(1)–C(2)	81.9(4)	82.0(3)	81.9(2)	82.2(4)	82.22(15)	82.7(2)
Se(1)–C(2)–N(2)	113.9(7)	114.7(5)	113.7(4)	112.9(6)	113.8(3)	113.5(4)
C(2)–N(2)–N(1)	114.5(8)	114.1(6)	115.1(4)	115.8(8)	115.1(3)	114.7(4)
N(2)–N(1)–C(1)	115.6(8)	116.5(6)	114.1(5)	114.0(8)	115.0(3)	116.8(4)
N(1)–C(1)–Se(1)	114.0(8)	112.6(5)	115.2(4)	115.0(7)	113.9(3)	112.2(4)

mately co-planar with the two aromatic substituents. This can be readily illustrated through a comparison of the torsion angles to the substituents which are all close to 180° [range 176.1(7)–180.0(8)°]. The C–Se bond lengths for all six compounds (ca. 1.87–1.89 Å) are similar to that of 2,5-diarylselenophenes (ca. 1.86–1.89 Å).[23] The distances in **2** are slightly shorter than those found in related structures containing single C–Se bonds (ca. 1.92–1.94 Å),[24] indicating that some slight delocalisation in **2**. However, the C–Se–C angles ranging between 81.9(2)–82.7(2)° in **2b**, **2h**, **2k**, **2m**, **2p** and **2s** are considerably smaller than that [ca. 87.7(7)–88.7(10)°] in 2,5-diarylselenophenes.[24]

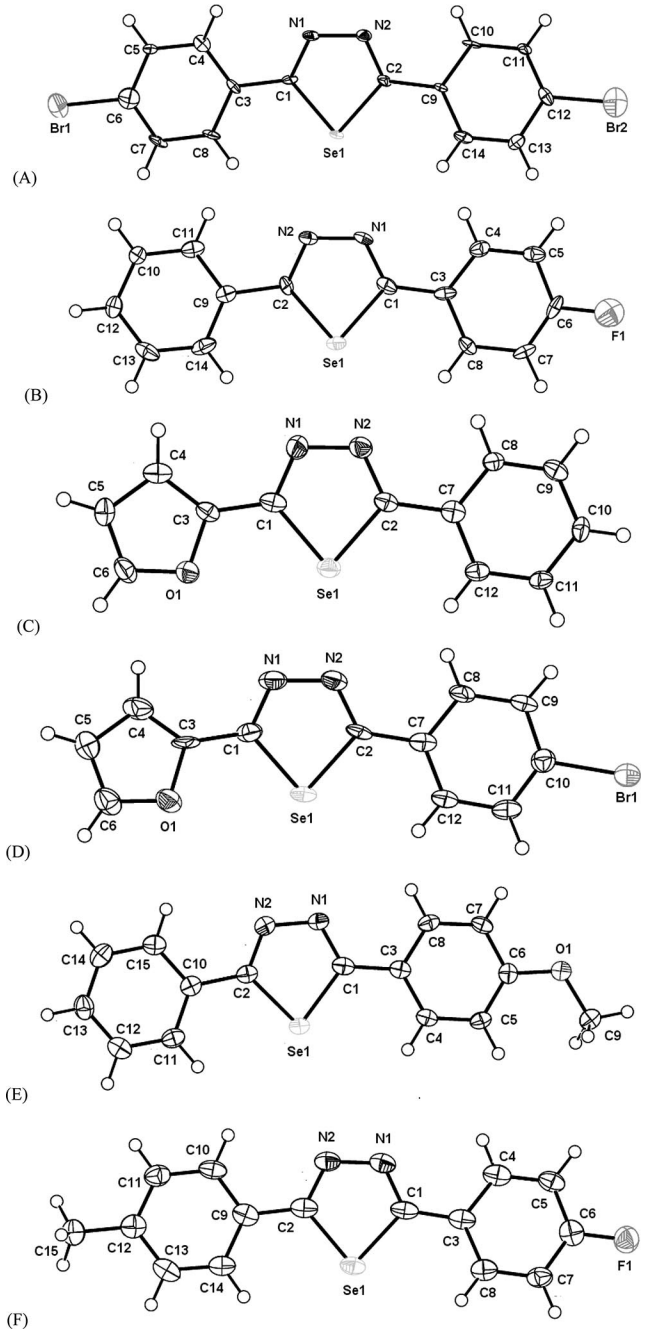


Figure 1. X-ray crystal structures of **2b** (A), **2h** (B), **2k** (C), **2m** (D), **2p** (E) and **2s** (F).

Conclusions

In summary, a highly efficient route for the preparation of a wide variety of 1,2-diacylhydrazines has been developed. The selenation of 1,2-diacylhydrazines using Woollins' reagent, 2,4-diphenyl-1,3-diselenadiphosphetane-2,4-diselenide, provides a general and systemic approach to 2,5-disubstituted 1,3,4-selenadiazoles. This method allows 2,5-disubstituted 1,3,4-selenadiazoles to be easily available for further investigations into their chemistry and biological properties.

Experimental Section

General: Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air. Solvents were dried, purified, and stored according to common procedures.

^{1}H (270 MHz), ^{13}C (67.9 MHz), ^{31}P{^{1}H} (109 MHz) and ^{77}Se-{^{1}H} (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} on a Perkin–Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St-Andrews microanalysis service. Mass spectrometry was performed by the University of St Andrews Mass Spectrometry Service. X-ray crystal data as Table 3 for compounds **2b**, **2g**, **2h**, **2k**, **2m**, **2p** and **2s** was collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were obtained with full-matrix least-squares based on F^2 by using SHELXTL.

CCDC-711573 (for **2b**), -711574 (for **2h**), -711575 (for **2k**), -711576 (for **2m**), -711577 (for **2p**), -711578 (for **2s**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Synthesis of 1,2-Diacylhydrazines 1a–t: A suspension of carbonyl hydrazide (10.0 mmol) and anhydrous sodium carbonate (1.02 g, 10.0 mmol) in dry tetrahydrofuran (60 mL) and water (60 mL) was added to a stirring solution of the corresponding carbonyl chloride (11.0 mmol) in 30 mL of tetrahydrofuran at 0 °C. The mixture was stirred at 0 °C for 1 h, and at room temperature for 4 h. A massive precipitation was observed. The product was harvested by filtration and washed three times with tetrahydrofuran and ethyl ether, then finally dried in vacuo.

***N′*-Benzoylbenzohydrazide (1a):** A white solid (61%, 1.45 g); m.p. 236–238 °C. Selected IR (KBr): $\tilde{\nu}$ = 3201 (s), 3001 (s), 1670 (m), 1633 (vs), 1579 (s), 1537 (s), 1487 (s), 1287 (s), 687 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): 10.53 (s, 2 H, NH), 7.94 (m, 4 H, H2, H6 ArH), 7.55 (m, 6 H, H3, H4, H5 ArH) . ^{13}C NMR ([D$_6$]DMSO): δ = 166.3 (C=O), 133.3, 132.4, 129.1, 128.0 ppm. MS (CI): *m*/*z* = 241 [M + H]$^+$.

4-Bromo-*N′*-(4-chlorobenzoyl)benzohydrazide (1b): A white solid (65%, 2.30 g); m.p. 302–303 °C. Selected IR (KBr): $\tilde{\nu}$ = 3187 (s), 3017 (w), 1601 (vs), 1561 (s), 1461 (s), 1264 (m), 1090 (m), 1010 (m), 848 (m), 742 (m), 659 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.66 (s, 2 H, NH), 7.95 [d, *J*(H,H) = 8.5 Hz, 2 H, ArH], 7.87 [d,

Table 3. Details of the X-ray data collections and refinements for **2b**, **2h**, **2k**, **2m**, **2p** and **2s**.

	2b	**2h**	**2k**	**2m**	**2p**	**2s**
Formula	$C_{14}H_8Br_2N_2Se$	$C_{14}H_9FN_2Se$	$C_{12}H_8N_2OSe$	$C_{12}H_7BrN_2OSe$	$C_{15}H_{12}N_2OSe$	$C_{15}H_{11}FN_2Se$
M	443.00	303.19	275.16	354.07	315.23	317.22
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$Pbca$	$P2_1/c$
a [Å]	15.421(6)	13.160(6)	7.217(3)	6.112(3)	14.222(6)	14.888(8)
b [Å]	14.353(5)	5.489(3)	13.857(5)	21.886(9)	6.056(3)	14.385(7)
c [Å]	6.121(2)	16.177(8)	10.474(3)	8.871(4)	29.774(15)	6.002(3)
β	101.091(10)	99.108(12)	90	103.712(10)	90	97.699(13)
U/A^3	1329.4(8)	1153.8(10)	1047.4(6)	1152.8(9)	2564(2)	1273.9(11)
Z	4	4	4	4	8	4
μ [mm]$^{-1}$	8.82	3.25	3.56	6.71	2.92	2.95
Reflections collected	8630	7127	7030	7733	15423	8122
Independent reflections	2678	2266	2152	2277	2582	2610
R_{int}	0.120	0.103	0.101	0.217	0.049	0.161
$R(F^2) > 2\sigma\ (F^2)$	0.094	0.075	0.048	0.098	0.045	0.086
$wR_2\ [I > 2\sigma(I)]$	0.273	0.252	0.114	0.308	0.088	0.227

J(H,H) = 8.5 Hz, 2 H, ArH], 7.75 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.62 [d, J(H,H) = 8.5 Hz, 2 H, ArH] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 165.5 (C=O), 165.4 (C=O), 137.4, 132.2, 132.1, 131.8, 130.1, 130.0, 129.3, 126.3 ppm. MS (ES$^+$): m/z = 377 [M + Na]$^+$. MS (ES$^-$): m/z = 353 [M – H]$^+$.

***N′*-Benzoylnicotinohydrazide (1c):** A white solid (77%, 1.85 g); m.p. 232–234 °C. Selected IR (KBr): $\tilde{\nu}$ = 3201 (m), 3003 (m), 1631 (s), 1537 (s), 1295 (s), 874 (m), 698 (s) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.69 (s, 2 H, NH), 9.09 (s, 1 H, PyH), 8.80 (d, 1 H, PyH), 8.29 (d, 1 H, PyH), 7.94 (m, 2 H, ArH), 7.57 (m, 4 H, PyH and ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.3 (C=O), 165.0 (C=O), 153.1, 149.0, 135.8, 133.0, 132.5, 129.1, 128.9, 128.0, 124.3 ppm. MS (CI): m/z = 242 [M + H]$^+$.

***N′*-(4-Methoxybenzoyl)nicotinohydrazide (1d):** A white solid (82%, 2.21 g); m.p. 126–128 °C. Selected IR (KBr): $\tilde{\nu}$ = 3203 (m), 3003 (m), 1632 (s), 1605 (s), 1503 (s), 1258 (s), 1175 (m), 1026 (m), 846 (w), 704 (w) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.66 (s, 2 H, NH), 9.10 (s, 1 H, PyH), 8.79 (d, 1 H, PyH), 8.30 (d, 1 H, PyH), 7.93 (m, 2 H, ArH), 7.58 (m, 1 H, PyH), 7.07 (m, 2 H, ArH), 3.84 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 165.9 (C=O), 165.1 (C=O), 153.1, 149.0, 135.8, 129.9, 128.9, 125.1, 124.3, 114.4, 114.0, 56.0 ppm. MS (CI): m/z = 272 [M + H]$^+$.

***N′*-Benzoyl-4-methylbenzohydrazide (1e):** A white solid (63%, 1.58 g); m.p. 219–221 °C. Selected IR (KBr): $\tilde{\nu}$ = 3202 (s), 3007 (s), 1631 (vs), 1578 (m), 1539 (s), 1489 (m), 1284 (s), 691 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.45 (s, 2 H, NH), 7.93 [d, J(H,H) = 7.7 Hz, 2 H, ArH], 7.84 [d, J(H,H) = 7.4 Hz, 2 H, ArH], 7.55 (m, 3 H, ArH), 7.32 [d, J(H,H) = 7.4 Hz, 2 H, ArH], 2.38 (s, 3 H, CH$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.4 (C=O), 166.2 (C=O), 142.4, 133.3, 132.4, 130.4, 129.6, 129.1, 128.0, 21.6 ppm. MS (CI): m/z = 255 [M + H]$^+$.

***N′*-Benzoyl-4-chlorobenzohydrazide (1f):** A white solid (67%, 1.96 g); m.p. 224–226 °C. Selected IR (KBr): $\tilde{\nu}$ = 3195 (s), 3010 (w), 2843 (w), 1599 (vs), 1564 (s), 1498 (m), 1461 (s), 1266 (m), 1089 (m), 1010 (m), 849 (m), 710 (m), 687 (m), 647 (m), 454 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.60 (s, 2 H, NH), 7.94 (m, 5 H, ArH), 7.55 (m, 4 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.4 (C=O), 165.4 (C=O), 137.3, 133.1, 132.5, 131.9, 130.0, 129.2, 129.1, 128.0 ppm. MS (ES$^+$): m/z = 297 [M + Na]$^+$. MS (ES$^-$): m/z = 273 [M – H]$^+$.

***N′*-Benzoyl-4-bromobenzohydrazide (1g):** A white solid (69%, 2.18 g); m.p. 207–209 °C. Selected IR (KBr): $\tilde{\nu}$ = 3192 (s), 3009 (w), 1600 (vs), 1576 (s), 1561 (s), 1461 (s), 1264 (s), 706 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.58 (s, 2 H, NH), 7.91 (m, 3 H, ArH), 7.77 (m, 2 H, ArH), 7.55 (m, 4 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.4 (C=O), 165.6 (C=O), 133.0, 132.5, 132.2, 130.1, 129.9, 129.1, 128.0, 126.3 ppm. MS (CI): = 319 [M + H]$^+$.

***N′*-Benzoyl-4-fluorobenzohydrazide (1h):** A white solid (81%, 2.06 g); m.p. 228–230 °C. Selected IR (KBr): $\tilde{\nu}$ = 3209 (s), 3011 (s), 1674 (s), 1635 (vs), 1605 (s), 1538 (s), 1504 (s), 1283 (s), 1240 (s), 1160 (m), 849 (m), 688 (m), 594 (m), 541 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.57 (s, 2 H, NH), 8.02 (m, 2 H, ArH), 7.95 (m, 2 H, ArH), 7.56 (m, 3 H, ArH), 7.38 (m, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.4 (C=O), 165.4 (C=O), 163.0, 133.1, 132.5, 139.7, 129.1, 128.0, 116.3, 116.0 ppm. MS (ES$^+$): m/z = 281 [M + Na]$^+$. MS (ES$^-$): m/z = 257 [M – H]$^+$.

***N′*-Benzoylthiophen-2-carbohydrazide (1i):** A white solid (70%, 1.72 g); m.p. 102–104 °C. Selected IR (KBr): $\tilde{\nu}$ = 3210 (m), 3020 (m), 1715 (m), 1652 (s), 1536 (s), 1270 (s), 709 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 9.80 (s, 2 H, NH), 9.81 (s, 2 H, NH), 9.00 (m, 3 H), 7.72 (m, 3 H), 7.13 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 161.7 (C=O), 139.0 (C=O), 130.9, 128.5, 128.0 ppm. MS (CI): m/z = 247 [M + H]$^+$.

Ethyl 2-Benzoylhydrazinecarboxylate (1j): A white paste (90%, 1.85 g); Selected IR (KBr): $\tilde{\nu}$ = 3208 (m), 3021 (m), 1711 (s), 1650 (s), 1530 (m), 1326 (m), 1267 (s), 707 (s) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 8.81 (s, 2 H, NH), 8.10 (m, 2 H, ArH), 7.80 (m, 1 H, ArH), 7.48 (m, 2 H, ArH), 4.14 [q, J(H,H) = 7.2 Hz, 2 H, OCH$_2$], 1.23 [t, J(H,H) = 7.2 Hz, 3 H, CH$_3$] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 171.1 (C=O), 167.3 (C=O), 133.7, 130.1, 127.4, 62.5, 14.2 ppm. MS (CI): m/z = 209 [M + H]$^+$.

***N′*-Benzoylfuran-2-carbohydrazide (1k):** A white solid (81%, 1.85 g); m.p. 208–210 °C. Selected IR (KBr): $\tilde{\nu}$ = 3198 (s), 1672 (m), 1634 (vs), 1592 (m), 1580 (m), 1525 (m), 1471 (m), 1291 (s), 1221 (m), 1159 (m), 1010 (m), 846 (m), 754 (m), 703 (m), 689 (m), 594 (m), 540 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.46 (s, 2 H, NH), 7.95 (m, 3 H, ArH), 7.55 (m, 3 H, ArH&FurH), 7.28 (d, 1 H, FurH), 6.69 (t, 1 H, FurH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.4 (C=O), 157.9 (C=O), 146.9, 146.4, 133.0, 132.5, 129.1, 128.0, 115.2, 112.5 ppm. MS (ES$^+$): m/z = 253 [M + Na]$^+$. MS (ES$^-$): m/z = 229 [M – H]$^+$.

***N′*-(4-Methylbenzoyl)furan-2-carbohydrazide (1l):** A white solid (65%, 1.57 g); m.p. 225–227 °C. Selected IR (KBr): $\tilde{\nu}$ = 3173 (m), 3011 (m), 1673 (m), 1631 (vs), 1592 (m), 1527 (m), 1504 (m), 1471

(m), 1286, 1217 (m), 1186 (m), 1120 (m), 1020 (m), 851 (m), 746 (s), 595 (s), 540 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.37 (s, 2 H, NH), 7.91 (d, 1 H, FurH), 7.81 [d, J(H,H) = 6.6 Hz, 2 H, ArH], 7.31 [d, J(H,H) = 6.6 Hz, 2 H, ArH], 7.26 (d, 1 H, FurH), 6.68 (m, 1 H, FurH), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.3 (C=O), 158.0 (C=O), 146.9, 146.3, 142.5, 130.2, 129.6, 128.1, 115.1, 112.4, 21.6 ppm. MS (ES^+): m/z (%) = 267 $[M + Na]^+$.

***N′*-(4-Bromobenzoyl)furan-2-carbohydrazide (1m):** A white solid (63%, 1.95 g); m.p. 191–193 °C. Selected IR (KBr): $\tilde{\nu}$ = 3167 (w), 3004 (w), 1637 (vs), 1592 (s), 1520 (m), 1483 (m), 1289 (m), 1010 (m), 840 (m), 747 (m), 594 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.57 (s, 2 H, NH), 7.94 [d, J(H,H) = 10.2 Hz, 1 H, FurH], 7.85 [d, J(H,H) = 8.2 Hz, 2 H, ArH], 7.74 [d, J(H,H) = 8.2 Hz, 2 H, ArH], 7.27 [d, J(H,H) = 10.2 Hz, 1 H, FurH], 6.69 (m, 1 H, FurH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 165.5 (C=O), 157.9 (C=O), 148.4, 146.4, 132.5, 132.2, 130.1, 126.3, 115.3, 112.5 ppm. MS (ES^+): m/z = 333 $[M + Na]^+$. MS (ES^-): m/z = 309 $[M - H]^+$.

4-Methoxy-*N′*-(4-methylbenzoyl)benzohydrazide (1n): A white solid (69%, 1.94 g); m.p. 214–216 °C. Selected IR (KBr): $\tilde{\nu}$ = 3214 (s), 3010 (w), 2844 (w), 1599 (vs), 1561 (m), 1512 (m), 1469 (m), 1440 (m), 1255 (s), 1177 (m), 1028 (m), 840 (m), 743 (m), 598 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.35 (s, 2 H, NH), 7.92 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.83 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.31 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.05 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 3.85 (s, 3 H, OCH_3), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 166.4 (C=O), 165.9 (C=O), 162.6, 142.4, 130.4, 129.9, 129.6, 128.0, 125.3, 114.3, 56.0, 21.6 ppm. MS (ES^+): m/z = 307 $[M + Na]^+$.

***N′*-Benzoyl-4-methoxybenzohydrazide (1p):** A white solid (77%, 2.07 g); m.p. 188–190 °C. Selected IR (KBr): $\tilde{\nu}$ = 3206 (s), 3005 (s), 1632 (s), 1607 (s), 1542 (m), 1505 (s), 1260 (s), 1175 (m), 1031 (m), 842 (m), 691 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.42 (s, 2 H, NH), 7.92 (m, 4 H, ArH), 7.55 (m, 3 H, ArH), 7.07 (m, 2 H, ArH), 3.41 (s, 3 H, OCH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.5 (C=O), 165.9 (C=O), 133.3, 132.4, 130.0, 129.1, 128.0, 125.3, 114.3, 56.0 (OCH_3) ppm. MS (CI): m/z = 271 $[M + H]^+$.

4-Chloro-*N′*-(4-methylbenzoyl)benzohydrazide (1r): A white solid (68%, 1.95 g); m.p. 255–256 °C. Selected IR (KBr): $\tilde{\nu}$ = 3193 (s), 3014 (w), 1599 (vs), 1563 (s), 1511 (m), 1463 (s), 1267 (m), 1225 (m), 1090 (m), 1012 (m), 850 (m), 741 (m), 663 (m), 603 (m), 462 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.53 (s, 2 H, NH), 7.94 [d, J(H,H) = 7.7 Hz, 2 H, ArH], 7.74 [d, J(H,H) = 7.2 Hz, 2 H, ArH], 7.61 [d, J(H,H) = 7.2 Hz, 2 H, ArH], 7.33 [d, J(H,H) = 7.7 Hz, 2 H, ArH], 2.38 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.3 (C=O), 165.4 (C=O), 142.5, 137.3, 131.9, 130.2, 130.0, 129.6, 129.3, 128.1, 21.6 ppm. MS (ES^+): m/z = 311 $[M + Na]^+$. MS (ES^-): m/z = 287 $[M - H]^+$.

4-Fluoro-*N′*-(4-methylbenzoyl)benzohydrazide (1s): A white solid (57%, 1.55 g); m.p. 224–225 °C. Selected IR (KBr): $\tilde{\nu}$ = 3202 (m), 3013 (w), 1605 (vs), 1584 (s), 1511 (m), 1461 (s), 1267 (m), 1225 (m), 1155 (m), 851 (m), 742 (m), 661 (m), 600 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.49 (s, 2 H, NH), 8.01 [d, J(H,H) = 6.3 Hz, 2 H, ArH], 7.83 [d, J(H,H) = 6.3 Hz, 2 H, ArH], 7.34 (m, 4 H, ArH), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 166.3 (C=O), 165.4 (C=O), 162.9, 142.5, 130.8, 130.7, 130.3, 129.6, 128.1, 116.3, 115.9, 21.6 ppm. MS (ES^+): m/z = 295 $[M + Na]^+$, 273 $[M + H]^+$.

4-Bromo-*N′*-(4-methoxybenzoyl)benzohydrazide (1t): A white solid (81%, 2.80 g); m.p. 240–242 °C. Selected IR (KBr): $\tilde{\nu}$ = 3209 (m), 3009 (w), 1600 (vs), 1560 (m), 1467 (s), 1255 (s), 1178 (m), 1031 (m), 847 (m), 744 (m), 609 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.54 (s, 2 H, NH), 7.90 (m, 4 H, ArH), 7.76 [d, J(H,H) = 7.7 Hz, 2 H, ArH], 7.05 [d, J(H,H) = 7.7 Hz, 2 H, ArH], 3.83 (s, 3 H, OCH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 165.9 (C=O), 165.6 (C=O), 162.6, 132.2, 130.1, 130.0, 126.2, 125.2, 114.3, 56.0 ppm. MS (ES^+): m/z = 371 $[M + Na]^+$.

General Procedure for the Synthesis of 2,5-Disubstituted 1,3,4-Selenadiazoles 2a-t: A mixture of 1,2-diacylhydrazines (1.0 mmol) and Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene was refluxed for 7 h. The red suspension disappeared and a brown suspension was formed along with some grey elemental selenium. After cooling to room temperature the mixture was dried in vacuo to remove toluene. The residue was then dissolved in dichloromethane and purified by silica gel (1:5 ethyl acetate/dichloromethane as eluent) to give the corresponding target product.

2,5-Diphenyl-1,3,4-selenadiazole (2a): A yellow solid (98%, 0.28 g); m.p. 116–118 °C. Selected IR (KBr): $\tilde{\nu}$ = 3424 (s), 1438 (m), 1149 (s), 933 (m), 691 (s), 543 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.95 (m, 4 H, ArH), 7.50 (m, 6 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 174.9 (C=N), 1431.2, 129.3, 128.7, 126.9 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 687.13 ppm. MS (CI): m/z = 287 $[M + H]^+$. $C_{14}H_{10}N_2Se$ (285.11): calcd. C 58.98, H 3.54, N 9.83; found C 59.30, H 3.85, N 9.79.

2,5-Bis(4-bromophenyl)-1,3,4-selenadiazole (2b): A yellow solid (75%, 0.33 g); m.p. 210 °C (dec.). Selected IR (KBr): $\tilde{\nu}$ = 3424 (w), 2921 (w), 1602 (s), 1544 (m), 1477 (vs), 1397 (m), 1266 (w), 1090 (s), 1072 (s), 1009 (s), 838 (s), 737 (s), 520 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.06 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.98 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.67 [d, J(H,H) = 8.5 Hz, 2 H, ArH], 7.51 [d, J(H,H) = 8.5 Hz, 2 H, ArH] ppm. ^{13}C NMR (CD_2Cl_2): δ = 164.1 (C=N), 151.7 (C=N), 138.3, 132.6, 130.1, 129.9, 129.6, 128.4, 128.3, 126.7, 122.7 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 690.60 ppm. MS (CI): m/z = 443 $[M + H]^+$. $C_{14}H_8Br_2N_2Se$ (442.91): calcd. C 37.96, H 1.82, N 6.32; found C 37.66, H 1.91, N 6.08.

2-Phenyl-5-(pyridine-3-yl)-1,3,4-selenadiazole (2c): A greenish yellow solid (51%, 0.15 g); m.p. 90–92 °C. Selected IR (KBr): $\tilde{\nu}$ = 3424 (s), 1454 (m), 1435 (m), 1127 (m), 1055 (m), 761 (m), 690 (s), 532 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.38 (s, 1 H, PyH), 8.13 (d, 1 H, PyH), 7.93 (m, 3 H, PyH & ArH), 7.57 (m, 4 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 149.5 (C=N), 147.6 (C=N), 137.3, 131.6, 129.4, 128.9, 127.0, 124.9 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 698.88 ppm. MS (CI): m/z = 287 $[M + H]^+$. $C_{13}H_9N_3Se$ (286.10): calcd. C 54.56, H 3.17, N 14.68; found C 54.10, H 3.61, N 14.57.

2-(4-Methoxyphenyl)-5-(pyridine-3-yl)-1,3,4-selenadiazole (2d): A yellow solid (58%, 0.18 g); m.p. 98–100 °C. Selected IR (KBr): $\tilde{\nu}$ = 3425 (m), 3049 (m), 1454 (m), 1434 (s), 1140 (m), 1081 (m), 958 (m), 761 (m), 690 (s), 534 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 9.54 (s, 1 H, PyH), 9.01 (d, 1 H, PyH), 8.88 (d, 1 H, PyH), 8.01 (m, 3 H, PyH & ArH), 7.47 (m, 4 H, PyH & ArH), 3.86 (s, 3 H, OCH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 144.0 (C=N), 142.6 (C=N), 132.0, 129.4, 129.0, 128.4, 128.2, 127.9, 127.2, 55.8 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 714.61 ppm. MS (CI): m/z = 318 $[M + H]^+$. $C_{14}H_{12}N_3OSe$ (317.14): calcd. C 53.18, H 3.51, N 13.29; found C 53.51, H 3.61, N 13.57.

2-Phenyl-5-*p*-tolyl-1,3,4-selenadiazole (2e): A yellow solid (90%, 0.27 g); m.p. 102–104 °C. Selected IR (KBr): $\tilde{\nu}$ = 2918 (w), 1607 (m), 1546 (m), 1494 (m), 1441 (s), 1258 (m), 1061 (s), 962 (m), 817 (s), 757 (m), 685 (s), 578 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.12 [d, J(H,H) = 7.2 Hz, 2 H, ArH], 7.83 [d, J(H,H) = 7.9 Hz, 2 H, ArH], 7.49 (m, 3 H, ArH), 7.27 [d, J(H,H) = 7.9 Hz, 2 H, ArH], 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 164.8 (C=N), 164.4 (C=N), 141.9, 131.6, 131.0, 129.9, 129.2, 128.4, 126.8, 21.4 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 683.01 ppm. MS (CI): m/z = 301 $[M + H]^+$. $C_{15}H_{12}N_2Se$ (300.02): calcd. C 60.21, H 4.04, N 9.36; found C 60.31, H 4.29, N 9.51.

2-(4-Chlorophenyl)-5-phenyl-1,3,4-selenadiazole (2f): A yellow solid (97%, 0.31 g); m.p. 198–199 °C. Selected IR (KBr): $\tilde{\nu}$ = 3424 (w), 1590 (m), 1494 (m), 1440 (vs), 1418 (s), 1238 (m), 1089 (s), 1062 (s), 1010 (m), 965 (m), 845 (m), 820 (m), 762 (s), 686 (m), 661 (m), 578 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.95 (m, 4 H, ArH), 7.47 (m, 5 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 136.9 (C=N), 133.1 (C=N), 131.7, 131.3, 129.9, 129.5, 129.3, 128.7 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 688.61 ppm. MS (ESI^+): *m*/*z* = 343 $[M + Na]^+$. $C_{14}H_9ClN_2Se$ (319.56): calcd. C 52.61, H 2.84, N 8.76; found C 52.56, H 2.49, N 8.49.

2-(4-Bromophenyl)-5-phenyl-1,3,4-selenadiazole (2g): A greenish yellow solid (95%, 0.35 g); m.p. 90–92 °C. Selected IR (KBr): $\tilde{\nu}$ = 3449 (w), 1583 (m), 1492 (m), 1439 (s), 1417 (m), 1256 (m), 1063 (s), 824 (s), 760 (s), 688 (s), 577 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.94 (d, 2 H, ArH), 7.83 (d, 2 H, ArH), 7.62 (m, 2 H, ArH), 7.50 (d, 3 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 164.8 (C=N), 164.0 (C=N), 132.5, 131.9, 131.3, 130.0, 129.3, 128.7, 128.3, 126.9 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 688.75 ppm. MS (CI): *m*/*z* = 365 $[M + H]^+$. $C_{14}H_9BrN_2Se$ (364.01): calcd. C 46.18, H 2.49, N 7.69; found C 46.96, H 2.28, N 7.78.

2-(4-Fluorophenyl)-5-phenyl-1,3,4-selenadiazole (2h): A greenish yellow solid (91%, 0.28 g); m.p. 102–104 °C. Selected IR (KBr): $\tilde{\nu}$ = 3427 (w), 3063 (w), 1606 (m), 1550 (m), 1495 (vs), 1445 (m), 1415 (m), 1234 (s), 1152 (m), 1072 (m), 844 (s), 734 (s), 687 (s), 616 (m), 523 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.15 (d, 2 H, ArH), 7.96 (d, 2 H, ArH), 7.53 (m, 3 H, ArH), 7.25 (m, 2 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 166.3 (C=N), 163.8 (C=N), 131.8, 131.2, 130.7, 129.2, 128.7, 126.8, 117.2, 116.2 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 686.62 ppm. MS (ESI^+): *m*/*z* (%) = 327 $[M + Na]^+$. $C_{14}H_9FN_2Se$ (303.10): calcd. C 55.46, H 2.99, N 9.24; found C 55.56, H 2.93, N 9.17.

2-Phenyl-5-(thiophen-2-yl)-1,3,4-selenadiazole (2i): A yellow oil (92%, 0.31 g). Selected IR (KBr): $\tilde{\nu}$ = 3430 (w), 3060 (w), 1608 (m), 1499 (s), 1447 (m), 1420 (m), 1240 (s), 1076 (m), 739 (s), 690 (s), 618 (m), 525 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.94 (m, 1 H, thiophen-H), 7.75–7.37 (m, 3 H, ArH), 7.03 (m, 2 H, ArH), 6.24 (m, 1 H, thiophen-H), 6.12 (m, 1 H, thiophen-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 166.6 (C=N), 164.0 (C=N), 131.3, 131.2, 130.8, 129.3, 128.7, 128.3, 127.6, 127.5, 127.1 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 688.24 ppm. MS (CI): *m*/*z* = 341 $[M + H]^+$. $C_{12}H_8N_2Se_2$ (337.94): calcd. C 42.63, H 2.39, N 8.28; found C 42.90, H 2.48, N 8.08.

2-Ethoxy-5-phenyl-1,3,4-selenadiazole (2j): A yellow paste (99%, 0.25 g). Selected IR (KBr): $\tilde{\nu}$ = 3056 (w), 2926 (w), 1757 (s), 1719 (s), 1690 (m), 1438 (m), 1369 (m), 1307 (m), 1281 (s), 1232 (s), 758 (m), 686 (s), 543 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.14 (m, 2 H, ArH), 7.54 (m, 3 H, ArH), 4.17 (t, 2 H, OCH_2), 1.25 (q, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 135.6 (C=N), 134.4 (C=N), 133.0, 132.4, 132.2, 131.3, 130.8, 64.1, 13.8 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 687.45 ppm. MS (CI): *m*/*z* = 255 $[M + H]^+$. $C_{10}H_{10}N_2OSe$ (253.07): calcd. C 47.44, H 3.98, N 11.07; found C 47.01, H 3.88, N 10.93.

2-(Furan-2-yl)-5-phenyl-1,3,4-selenadiazole (2k): A yellow solid (82%, 0.23 g); m.p. 100–102 °C. Selected IR (KBr): $\tilde{\nu}$ = 3137 (m), 1634 (m), 1582 (m), 1487 (s), 1453 (s), 1421 (m), 1259 (m), 1222 (m), 1058 (m), 1018 (s), 879 (s), 763 (vs), 750 (vs), 689 (vs), 658 (s), 588 (s), 557 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.94 (m, 2 H, ArH), 7.64 (d, 1 H, FurH), 7.47 (m, 3 H, ArH), 7.17 (d, 1 H, FurH), 6.61 (m, 1 H, FurH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 145.9 (C=N), 145.4 (C=N), 131.9, 131.2, 129.3, 128.7, 126.9, 114.0, 112.8, 112.2, 110.9 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 692.12 ppm. MS (ESI^+): *m*/*z* = 299 $[M + Na]^+$. $C_{12}H_8N_2OSe$ (275.08): calcd. C 52.38, H 2.93, N 10.18; found C 52.34, H 2.81, N 10.27.

2-(Furan-2-yl)-5-*p*-tolyl-1,3,4-selenadiazole (2l): A yellow solid (90%, 0.24 g); m.p. 98–100 °C. Selected IR (KBr): $\tilde{\nu}$ = 3449 (w), 3104 (w), 2896 (w), 1607 (m), 1492 (m), 1443 (s), 1261 (m), 1061 (m), 1017 (s), 880 (m), 819 (s), 754 (s), 596 (m), 558 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.79 (m, 3 H), 7.26 (m, 3 H), 6.61 (m, 1 H), 2.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 174.1 (C=N), 163.0 (C=N), 145.8, 145.2, 141.9, 129.9, 128.5, 112.7, 110.7, 21.3 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 688.42 ppm. MS (ESI^+): *m*/*z* = 313 $[M + Na]^+$. $C_{13}H_{10}N_2OSe$ (289.10): calcd. C 57.15, H 3.69, N 10.25; found C 56.75, H 3.54, N 10.14.

2-(4-Bromophenyl)-5-(furan-2-yl)-1,3,4-selenadiazole (2m): A yellow solid (96%, 0.34 g); m.p. 138–140 °C. Selected IR (KBr): $\tilde{\nu}$ = 3449 (m), 2920 (w), 2848 (w), 1586 (m), 1489 (s), 1445 (s), 1391 (m), 1254 (m), 1217 (m), 1055 (m), 1018 (m), 879 (m), 815 (s), 743 (s), 591 (m), 554 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.80 (d, 2 H, ArH), 7.61 (d, 2 H, ArH), 7.78 (d, 1 H, FurH), 7.19 (d, 1 H, FurH), 6.61 (m, 1 H, FurH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 172.7 (C=N), 163.8 (C=N), 146.1, 145.5, 132.5, 130.0, 128.4, 125.4, 112.9, 111.1 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 693.47 ppm. MS (CI): *m*/*z* = 355 $[M + H]^+$. $C_{12}H_7BrN_2OSe$ (353.97): calcd. C 40.71, H 1.99, N 7.91; found C 40.96, H 1.92, N 8.01.

2-(4-Methoxyphenyl)-5-*p*-tolyl-1,3,4-selenadiazole (2n): A yellow solid (90%, 0.29 g); m.p. 178–180 °C. Selected IR (KBr): $\tilde{\nu}$ = 3450 (w), 2961 (w), 1603 (s), 1513 (m), 1452 (s), 1407 (m), 1307 (m), 1256 (vs), 1177 (m), 1065 (m), 1034 (m), 836 (s), 817 (s), 606 (m), 578 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.85 (m, 4 H, ArH), 7.27 [d, *J*(H,H) = 7.7 Hz, 2 H, ArH], 6.96 [d, *J*(H,H) = 7.7 Hz, 2 H, ArH], 3.85 (s, 3 H, OCH_3), 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 174.0 (C=N), 162.0 (C=N), 141.7, 130.5, 130.2, 129.9, 128.5, 126.0, 114.5, 55.6, 21.3 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 673.66 ppm. MS (ESI^+): *m*/*z* = 353 $[M + Na]^+$. $C_{16}H_{14}N_2OSe$ (329.17): calcd. C 58.37, H 4.29, N 8.51; found C 58.51, H 3.86, N 8.19.

2-(4-Methoxyphenyl)-5-phenyl-1,3,4-selenadiazole (2p): A yellow solid (86%, 0.27 g); m.p. 130–132 °C. Selected IR (KBr): $\tilde{\nu}$ = 2936 (w), 2831 (w), 1604 (s), 1513 (m), 1438 (s), 1253 (vs), 1178 (m), 1034 (m), 763 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.91 (m, 4 H, ArH), 7.48 (m, 3 H, ArH), 6.99 (m, 2 H, ArH), 3.85 (s, 3 H, OCH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 174.5 (C=N), 173.9 (C=N), 133.3, 131.0, 130.2, 129.2, 128.6, 126.3, 125.9, 114.6, 55.6 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 677.36 ppm. MS (CI): *m*/*z* = 317 $[M + H]^+$. $C_{15}H_{12}N_2OSe$ (315.14): calcd. C 57.15, H 3.04, N 8.89; found C 56.54, H 3.62, N 8.94.

2-(4-Chlorophenyl)-5-*p*-tolyl-1,3,4-selenadiazole (2r): A yellow solid (83%, 0.27 g); m.p. 184–186 °C. Selected IR (KBr): $\tilde{\nu}$ = 3453 (w), 3074 (w), 2914 (w), 1601 (m), 1588 (m), 1441 (s), 1431 (s), 1396 (m), 1261 (m), 1073 (m), 817 (vs), 577 (m), 470 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.05 (m, 4 H, ArH), 7.51 [d, *J*(H,H) = 6.9 Hz, 2 H, ArH], 7.34 [d, *J*(H,H) = 6.9 Hz, 2 H, ArH], 2.48 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 164.9 (C=N), 163.6 (C=N), 142.7, 137.7, 129.9, 129.5, 128.6, 128.1, 126.8, 122.8, 21.4 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 684.21 ppm. MS (ESI): *m*/*z* = 357 $[M + Na]^+$. $C_{15}H_{11}ClN_2Se$ (333.59): calcd. C 53.99, H 3.32, N 8.40; found C 54.06, H 3.28, N 8.78.

2-(4-Fluorophenyl)-5-*p*-tolyl-1,3,4-selenadiazole (2s): A greenish yellow solid (79%, 0.25 g); m.p. 149–151 °C. Selected IR (KBr): $\tilde{\nu}$ = 3062 (w), 2920 (w), 1607 (m), 1494 (vs), 1228 (s), 1158 (m), 1069 (m), 1012 (m), 963 (m), 846 (m), 818 (m), 741 (m), 638 (m), 500 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.10 (m, 4 H, ArH), 7.27 (m, 4

H, ArH), 2.61 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 166.6 (C=N), 163.0 (C=N), 142.6, 130.7, 129.9, 129.2, 128.6, 126.8, 116.6, 116.2, 21.4 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 682.36 ppm. MS (ESI^+): *m/z* = 341 $[M + Na]^+$. $C_{15}H_{11}FN_2Se$ (317.13): calcd. C 56.79, H 3.50, N 8.83; found C 56.66, H 3.28, N 8.98.

2-(4-Bromophenyl)-5-(4-methoxyphenyl)-1,3,4-selenadiazole (2t): A yellow solid (75%, 0.30 g); m.p. 148–150 °C. Selected IR (KBr): $\tilde{\nu}$ = 2966 (w), 2838 (w), 1615 (s), 1494 (s), 1478 (m), 1307 (m), 1258 (s), 1126 (m), 1076 (m), 1029 (m), 1009 (m), 839 (s), 742 (s), 503 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.03 (m, 4 H, ArH), 7.68 [d, *J*(H,H) = 8.8 Hz, 2 H, ArH], 7.04 [d, *J*(H,H) = 8.8 Hz, 2 H, ArH], 3.87 (s, 3 H, OCH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 166.2 (C=N), 163.5 (C=N), 132.4, 130.3, 128.6, 128.2, 126.0, 123.2, 116.3, 114.6, 55.6 ppm. ^{77}Se NMR (CD_2Cl_2): δ = 678.61 ppm. MS (CI): *m/z* = 395 $[M + H]^+$. $C_{15}H_{11}BrN_2OSe$ (394.04): calcd. C 45.71, H 2.81, N 7.11; found C 45.96, H 2.68, N 7.31.

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