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# SYNTHESIS OF SELENOSEMICARBAZIDES AND 1,2,4-TRIAZOLES

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**Abstract** – Acyl isoselenocyanates (**1**) were prepared from KSeCN and acyl chlorides in situ. Reactions of the acyl isoselenocyanates (**1**) with phenylhydrazine gave 2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**) and selenosemicarbazides (**3**). The obtained selenosemicarbazides (**3**) were refluxed in the presence of triethylamine in THF and trapped with alkyl halides to obtain the corresponding 3-alkylseleno-1-phenyl-1*H*-1,2,4-triazoles (**5**) in moderate yields.

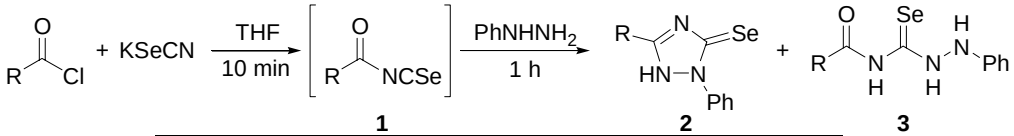
## INTRODUCTION

Several works on reactions of acyl isothiocyanates with hydrazines have been described in the literatures.[1] 4-Benzoyl-1-phenylthiosemicarbazide was obtained as the main product from the reaction of benzoyl isothiocyanate with phenylhydrazine. Using an excess of hydrazine in an alcoholic solvent, a mixture of triazolethione and benzoylhydrazide was afforded. With equimolar quantities of reactants, the reaction gave 1,4-dibenzoylthiosemicarbazide and its salt with hydrazine. In contrast, reactions of acyl isoselenocyanates with hydrazines have little been studied, though reactions with amines have been reported.[2] We confirmed that reactions of the acyl isoselenocyanates with phenylhydrazine afforded 2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**) and selenosemicarbazides (**3**). The treatment of selenosemicarbazides (**3**) with alkyl halides in the presence of triethylamine gave the corresponding 3-alkylseleno-1-phenyl-1*H*-1,2,4-triazoles (**5**). Herein, we report the reactions of the acyl isoselenocyanates with phenylhydrazine and synthesis of novel compounds (**2**) and (**5**).

## RESULTS AND DISCUSSION

Acyl isoselenocyanates (**1**) were prepared by reactions of acyl chloride with KSeCN as intermediate.[3] Reactions of five kinds of acyl isoselenocyanates (**1**) with phenylhydrazine were carried out at room temperature or -80°C for 1 h to afford 4-acyl-1-phenylselenosemicarbazides (**3**) as major products and 2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**)[4] as minor ones, respectively. The reactions at -80°C gave (**3**) in moderate yields. The reactions at room temperature afforded a mixture of products (**2**) and (**3**) except the reaction with pivaloyl isoselenocyanate (Table 1). The structure of **3** was confirmed by X-Ray crystal structure. In the case of acetyl, propionyl and butyryl isoselenocyanates, though the products (**2**) and (**3**) were confirmed formation in the reaction mixture from the result of TLC monitoring, they could not be isolated due to the decomposition during the process of purification by a silica gel column chromatography. In the case of reactions of isothiocyanates with hydrazine, similar reactions afforded different structures, 1,2,4-triazoline-3-thione[1g] or 1,2,4-triazoline-3-thiol as sole product.[1b,1e,5] In the present reaction, the selenosemicarbazides (**3**) were formed major product instead of cyclic compound (**2**). Pedersen reported the preparation of selenosemicarbazides by the reaction of alkyl isoselenocyanates with hydrazine in ethanol.[6] But the reactions did not give cyclic compound, 1,2,4-triazoline-3-selone.

**Table 1** Reaction of acyl isoselenocyanates with phenylhydrazine




| R | Reaction Temp. | Yield (%)[a] | |
|---|---|---|---|
| | | **2** | **3** |
| *p*-$CH_3C_6H_4$ (**a**) | rt | 38 | 23 |
| | -80°C | trace | 48 |
| $C_6H_5$ (**b**) | rt | 5 | 5 |
| | -80°C | trace | 32 |
| *p*-$CH_3OC_6H_4$ (**c**) | rt | 15 | 27 |
| | -80°C | trace | 41 |
| *p*-$ClC_6H_4$ (**d**) | rt | 20 | 16 |
| | -80°C | trace | 17 |
| *t*-Bu (**e**) | rt | 0 | 30 |
| | -80°C | 0 | 12 |

a: Isolated yield.

The X-Ray crystal structure of 1-phenyl-4-*p*-toluoylselenosemicarbazide (**3a**) was studied. An ORTEP drawing, depicted in Figure 1, shows the crystal structure of **3a**.[7] The sum of the three angles around each of the C1 and C2 atoms was 359.9°, the torsion angles of Se1-C1-N1-N2, Se1-C1-N3-C2, C1-N3-C2-O1 and C1-N3-C2-C3 were 3.0°, -166.9°, -1.3° and 179.2°, respectively, showing that the arrangement of

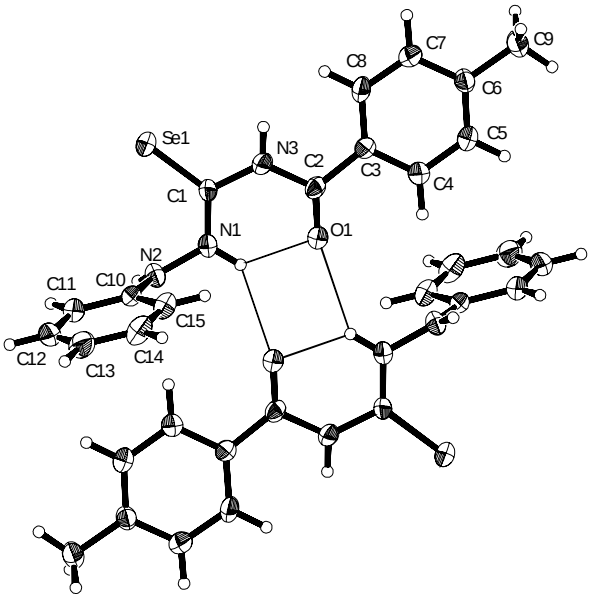
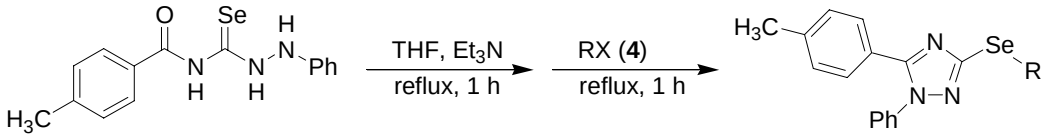
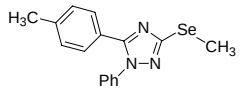
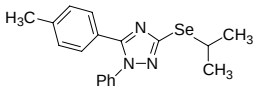
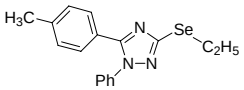
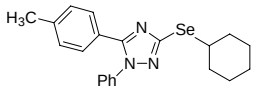
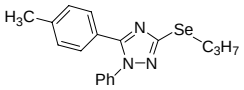
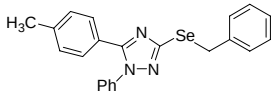
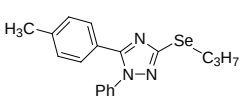
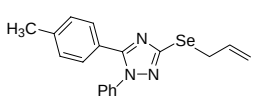



**Figure 1** X-Ray crystal structure of **3a**.

**Table 2** Synthesis of 3-alkylseleno-1*H*-1,2,4-triazoles (**5**) from 1-phenyl-4-*p*-toluoylselenosemicarbazides (**3a**)



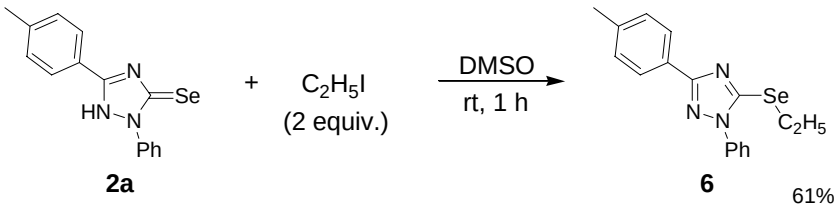

**3a** **5**

| RX **4** | Product **5** | Yield (%)[a] | RX **4** | Product **5** | Yield (%)[a] |
|---|---|---|---|---|---|
| $CH_3I$ |  **5a** | 70 | $(CH_3)_2CHI$ |  **5d** | 61 |
| $C_2H_5I$ |  **5b** | 86 | $cycloC_6H_{11}I$ |  **5e** | 55 |
| *n*-$C_3H_7I$ |  **5c** | 71 | BnBr |  **5f** | 61 |
| *n*-$C_3H_7Br$ |  **5c** | 35 | $CH_2$=$CHCH_2Br$ |  **5g** | 59 |

a: Isolated yield.

N2, N1, C1, Se1, N3, C2 and C3 atoms was almost planar. The four C-N bond and a N-N bond lengths of C10-N2 (1.406(9) Å) N1-N2 (1.404(7) Å), C1-N1 (1.292(9) Å), N3-C1 (1.402(8) Å) and C2-N3 (1.409(8) Å) in **3a** are shorter than the typical value of 1.47 Å.[8] These results can be attributed to the delocalization of π electrons and lone pair electrons on nitrogen atoms. The nitrogen atoms in **3a** has $sp^2$ rather than $sp^3$ character. Both inter- and intramolecular hydrogen bonds were observed (Figure 1). It is shown that the flexibility of the molecule is restricted by H-bonding between hydrogen atom on N1 atom and the O1 atom.

Cyclization of 1-phenyl-4-*p*-toluoylselenosemicarbazides (**3a**) in the presence of triethylamine was proceeded then trapped by alkyl halides (**4**) at reflux and led to moderate yields of seven different 3-alkylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazoles (**5**) (Table 2). In the case of 1-alkyl-4-phenylthiosemicarbazides, similar reaction afforded 1,2,4-triazole-3-thiol.[1b,1e] In the present reaction, the corresponding 1,2,4-triazole-3-selenol could not be isolated because of instability of the selenol, therefore, alkyl halides (**4**) was used as a trapping reagent to afford cyclic compound (**5**). In order to compare the structure of 2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**) with one of 3-alkylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazoles (**5**), reaction of 2-phenyl-5-*p*-tolyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selone (**2a**) with ethyl iodide was carried out. The reaction afforded 3-ethylseleno-2-phenyl-5-*p*-tolyl-2*H*-1,2,4-triazole (**6**) in 61% yield (Scheme 1).

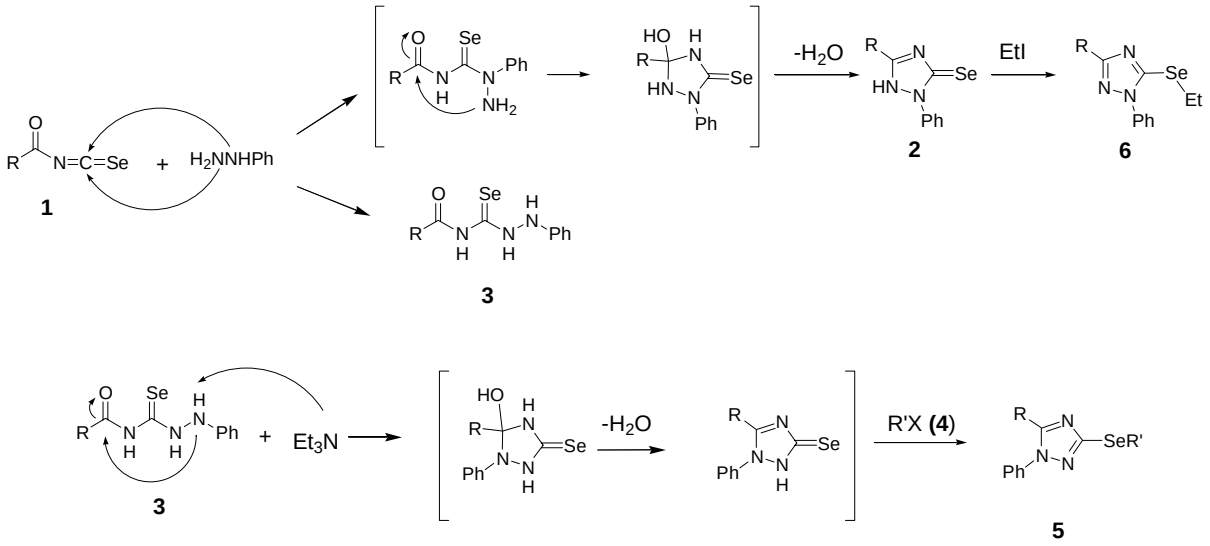



**2a** **6** 61%

**SCHEME 1**

From the $^1$H-, $^{13}$C- and $^{77}$Se NMR data, the difference of structures between compounds (**5**) and (**6**) was confirmed. The $^{13}$C NMR spectra of compound (**6**) shows the peaks for triazole ring carbons at 146.1 ppm and 163.1 ppm, while the corresponding signals of compound (**5b**) are at 153.8 ppm and 155.0 ppm. The $^{77}$Se NMR chemical shifts of **5** and **6** are observed at 270.8 ppm and 290.7 ppm, respectively. The results indicated that both compounds are different structures. From these results, the formations of products (**2**), (**3**) and (**5**) could be explained by the mechanism described in Scheme 2. The formation of **2** is initiated on the nucleophilic addition of phenylate amine of phenylhydrazine to isoselenocyanate carbon of **1**, affording the 2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**), whereas the formation of **3** is initiated on the nucleophilic addition of terminal amine of the phenylhydrazine to isoselenocyanate carbon of **1**, affording the 1-phenylselenosemicarbazides (**3**). The formation of **5** is initiated on the intramolecular

nucleophilic addition of nitrogen atom to carbonyl carbon of **3**, affording the 3-alkylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazoles (**5**). Thus, products (**2**) and (**5**) are obtained as the products bearing phenyl group at different position.




**SCHEME 2**

In conclusion, reactions of the acyl isoselenocyanates (**1**) with phenylhydrazine gave 1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**) and selenosemicarbazides (**3**), respectively. The obtained selenosemicarbazides (**3**) were used as starting materials for the synthesis of heterocycles to afford the corresponding 3-alkylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazoles (**5**) whereas 1,2-dihydro-3*H*-1,2,4-triazole-3-selones (**2**) was used for the synthesis of 3-ethylseleno-2-phenyl-5-*p*-tolyl-2*H*-1,2,4-triazole (**6**).

## EXPERIMENTAL

General

The $^{77}$Se chemical shifts were expressed in ppm deshielded with respect to neat $Me_2Se$ in $CDCl_3$ or DMSO.

**Synthesis of 2-phenyl-5-*p*-tolyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selone (2a) and 1-phenyl-4-*p*-toluoylselenosemicarbazide (3a).** To a solution of KSeCN (0.28 g, 2 mmol) in dry THF (5 mL) *p*-toluoyl chloride (0.13 mL, 1 mmol) in dry THF (5 mL) was added dropwise for 5 min at ambient temperature with stirring. The mixture was stirred for 10 min. Phenylhydrazine (0.10 mL, 1 mmol) in dry THF (5 mL) was added to the above mixture and stirred for 15 min. The reaction mixture was extracted with dichloromethane and washed with water. The combined organic layer was dried over sodium sulfate and evaporated to dryness. The residue was diluted with ether and the solid triazole (**2a**) (0.12 g, 38 %)

was recovered by filtration. mp 160.1-161.0ºC; IR (KBr): 3056, 1598, 1505, 1463, 1243 $cm^{-1}$; $^1H$ NMR (500 MHz, DMSO): δ 2.38 (s, 3H), 7.36 (d, 2H, *J* = 7.6 Hz), 7.49 (t, 1H, *J* = 7.6 Hz), 7.57 (t, 2H, *J* = 7.6 Hz), 7.93 (d, 2H, *J* = 7.6 Hz), 8.04 (d, 2H, *J* = 7.6 Hz), 14.7 (brs, 1H); $^{13}C$ NMR (125 MHz, DMSO): δ 21.1, 121.7, 124.7, 126.2, 128.3, 128.7, 129.7, 138.1, 141.3, 151.5, 158.5; $^{77}Se$ NMR (75 MHz, DMSO): δ 88.7; MS (FAB): *m/z* = 316 $[M+1]^+$; HRMS: *m/z* = 315.0275, Calcd. for $C_{15}H_{13}N_3Se$, Found 315.0316. The ether layer was evaporated to dryness. The residue was purified by flash column chromatography on silica gel using *n*-hexane: dichloromethane (1:1) as eluent to give **3a** (0.08 g, 23%). mp 137.1-139.8ºC; IR (KBr): 3230, 1670, 1604, 1492, 1264 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 2.46 (s, 3H), 6.96 (d, 2H, *J* = 8.0 Hz), 7.01 (t, 1H, *J* = 7.5 Hz), 7.26-7.34 (m, 4H), 7.43 (brs, 1H), 7.78 (d, 2H, *J* = 8.0 Hz), 9.40 (brs, 1H), 12.8 (brs, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 21.7, 114.6, 122.5, 127.7, 127.9, 129.4, 129.9, 145.09, 145.14, 166.8, 177.5; $^{77}Se$ NMR (75 MHz, $CDCl_3$): δ 296.8; MS (CI): *m/z* = 334 $[M+1]^+$; Anal. Calcd for $C_{15}H_{15}N_3OSe$: C, 54.22; H, 4.55; N, 12.65. Found: C, 53.80; H, 4.64; N, 12.50.

**2,5-Diphenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selone (2b)** mp 151.7-152.0ºC; IR (KBr): 3060, 1560, 1470, 1240 $cm^{-1}$; $^1H$ NMR (500 MHz, DMSO): δ 7.47 (t, 1H, *J* = 7.7 Hz), 7.51-7.59 (m, 5H), 7.98-8.05 (m, 4H), 14.7 (brs, 1H); $^{13}C$ NMR (125 MHz, DMSO): δ 124.5, 124.9, 126.3, 128.5, 128.7, 129.2, 131.3, 138.1, 151.5, 158.7; $^{77}Se$ NMR (75 MHz, DMSO): δ 89.8; MS (FAB): *m/z* = 302 $[M+1]^+$; HRMS: *m/z* = 301.0118, Calcd. for $C_{14}H_{11}N_3Se$, Found 301.0129.

**4-Benzoyl-1-phenylselenosemicarbazide (3b)** mp 123.4-125.7ºC; IR (KBr): 3181, 1679, 1600, 1514, 1474, 1263 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 6.95 (d, 2H, *J* = 7.6 Hz), 7.00 (t, 1H, *J* = 7.6 Hz), 7.29 (t, 2H, *J* = 7.6 Hz), 7.44 (d, 1H, *J* = 8.4 Hz), 7.50 (t, 2H, *J* = 7.6 Hz), 7.63 (t, 1H, *J* = 7.6 Hz), 7.86 (d, 2H, *J* = 7.6 Hz), 9.45 (brs, 1H), 12.8 (d, 2H, *J* = 7.6 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 114.7, 122.6, 127.7, 129.3, 129.4, 130.8, 134.0, 145.1, 166.9, 177.4; $^{77}Se$ NMR (75 MHz, $CDCl_3$): δ 303.4; MS (EI): *m/z* = 319 $[M]^+$; Anal. Calcd for $C_{14}H_{13}N_3OSe$: C, 52.84; H, 4.12; N, 13.20. Found: C, 52.54; H, 4.21; N, 13.16.

**5-*p*-Methoxyphenyl-2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selone (2c)** mp 146.1-147.6ºC; IR (KBr): 3006, 1614, 1508, 1458, 1241 $cm^{-1}$; $^1H$ NMR (500 MHz, DMSO): δ 3.84 (s, 3H), 7.12 (d, 2H, *J* = 8.6 Hz), 7.48 (t, 1H, *J* = 7.7 Hz), 7.56 (t, 2H, *J* = 7.7 Hz), 7.98 (d, 2H, *J* = 8.6 Hz), 8.03 (d, 2H, *J* = 7.7 Hz), 14.3 (brs, 1H); $^{13}C$ NMR (125 MHz, DMSO): δ 55.5, 114.7, 116.7, 124.8, 128.0, 128.3, 128.7, 138.1, 151.4, 158.3, 161.5; $^{77}Se$ NMR (75 MHz, DMSO): δ 87.2; MS (FAB): *m/z* = 332 $[M+1]^+$; HRMS: *m/z* = 331.0224, Calcd. for $C_{15}H_{13}N_3OSe$, Found 331.0212.

**4-*p*-Anisoyl-1-phenylselenosemicarbazide (3c)** mp 152.1-153.6ºC; IR (KBr): 3237, 1665, 1602, 1498, 1254 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.93-7.03 (m, 5H), 7.29 (t, 2H, *J* = 7.7 Hz), 7.42 (d, 1H, *J* = 7.7 Hz), 7.84 (d, 2H, *J* = 8.6 Hz), 9.32 (brs, 1H), 12.8 (brs, 1H, *J* = 7.6 Hz); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 55.6, 114.5, 114.6, 122.4, 122.6, 129.4, 129.9, 145.2, 164.2, 166.3, 177.6; $^{77}Se$ NMR (75

MHz, $CDCl_3$): δ 293.9; MS (EI): *m/z* = 349 $[M]^+$; Anal. Calcd for $C_{15}H_{15}N_3O_2Se$: C, 51.73; H, 4.34; N, 12.07. Found: C, 51.50; H, 4.40; N, 12.01.

**5-*p*-Chlorophenyl-2-phenyl-1,2-dihydro-3*H*-1,2,4-triazole-3-selone (2d)** mp 167.5-169.0ºC; IR (KBr): 3062, 1608, 1500, 1454, 1239 $cm^{-1}$; $^1H$ NMR (500 MHz, DMSO): δ 7.50 (t, 1H, *J* = 7.9 Hz), 7.57 (t, 2H, *J* = 7.9 Hz), 7.65 (dd, 2H, *J* = 1.8, 8.8 Hz), 8.01 (d, 2H, *J* = 7.9 Hz), 8.04 (d, 2H, *J* = 8.8 Hz), 14.8 (brs, 1H); $^{13}C$ NMR (125 MHz, DMSO): δ 124.5, 124.9, 126.3, 128.5, 128.8, 129.2, 131.3,138,1, 151.5, 158.8; $^{77}Se$ NMR (75 MHz, DMSO): δ 88.7; MS (FAB): *m/z* = 335 $[M+1]^+$; HRMS: *m/z* = 334.9728, Calcd. for $C_{14}H_{10}N_3ClSe$, Found 334.9759.

**4-*p*-Chlorobenzoyl-1-phenylselenosemicarbazide (3d)** mp 137.2-138.9ºC; IR (KBr): 3178, 1670, 1595, 1259 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 6.95 (d, 2H, *J* = 7.6 Hz), 7.02 (t, 1H, *J* = 7.6 Hz), 7.30 (t, 2H, *J* = 7.6 Hz), 7.42 (brs, 1H), 7.49 (t, 2H, *J* = 8.4 Hz), 7.82 (d, 2H, *J* = 8.4 Hz), 9.41 (brs, 1H), 12.7 (brs, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 114.6, 122.6, 129.09, 129.14, 129.4, 129.6, 140.6, 145.0, 165.9, 177.2; $^{77}Se$ NMR (75 MHz, $CDCl_3$): δ 309.3; MS (CI): *m/z* = 354 $[M+1]^+$; Anal. Calcd for $C_{14}H_{12}N_3OClSe$: C, 47.68; H, 3.43; N, 11.91. Found: C, 47.35; H, 3.49; N, 11.80.

**1-Phenyl-4-pivaloylselenosemicarbazide (3e)** mp 84.4-85.8ºC; IR (KBr): 3224, 1680, 1502, 1187 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 9H), 6.91 (d, 2H, *J* = 7.9 Hz), 6.99 (t, 1H, *J* = 7.9 Hz), 7.28 (t, 2H, *J* = 7.9 Hz), 7.40 (brs, 1H), 8.75 (brs, 1H), 12.6 (brs, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 26.8, 39.7, 114.6, 122.4, 129.3, 145.0, 177.1, 179.3; $^{77}Se$ NMR (75 MHz, $CDCl_3$): δ 288.3; MS (CI): *m/z* = 300 $[M+1]^+$; Anal. Calcd for $C_{12}H_{17}N_3OSe$: C, 48.33; H, 5.75; N, 14.09. Found: C, 47.98; H, 5.71; N, 13.96.

**Synthesis of 3-methylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5a)** To a solution of **3a** (0.17 g, 0.5 mmol) in dry THF (5 mL), triethylamine (0.07 mL, 0.5 mmol) was added and the reaction mixture was refluxed for 1 h. MeI (**4a**) (0.06 mL, 1 mmol) was added to the reaction mixture, and the mixture was stirred at reflux for 1h. The reaction mixture was extracted with diethyl ether and washed with saturated NaCl solution. The combined organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash column chromatography on silica gel using *n*-hexane: ether (2:1) as eluent to give **5a** (0.11 g, 70%). mp 113.0-114.1ºC; IR (KBr): 1501, 1459, 1260 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.56 (s, 3H, $^2J_{77Se\text{-}1H}$ = 11.5 Hz), 7.12 (d, 2H, *J* = 8.0 Hz), 7.32-7.44 (m, 7H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 6.1, 21.4, 124.6, 125.3, 128.71, 128.75, 129.2, 129.3, 138.1, 140.3, 154.2, 155.2; $^{77}Se$ NMR (75 MHz, $CDCl_3$): δ 158.7; MS (EI): *m/z* = 329 $[M]^+$; Anal. Calcd for $C_{16}H_{15}N_3Se$: C, 58.54; H, 4.61; N, 12.80. Found: C, 58.61; H, 4.85; N, 12.52.

**3-Ethylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5b)** mp 95.1-95.4ºC; IR (KBr): 1496, 1450, 1258 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.60 (t, 3H, *J* = 7.9 Hz), 2.34 (s, 3H), 3.23 (q, 2H, *J* = 7.9 Hz), 7.12 (d, 2H, *J* = 7.9 Hz), 7.32-7.43 (m, 7H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 16.0, 20.4, 21.3, 124.6, 125.3,

128.7, 129.16, 129.24, 138.1, 140.2, 153.8, 155.0; $^{77}$Se NMR (75 MHz, $CDCl_3$): δ 270.8; MS (EI): *m/z* = 343 $[M]^+$; Anal. Calcd for $C_{17}H_{17}N_3Se$: C, 59.65; H, 5.01; N, 12.28. Found: C, 59.24; H, 5.09; N, 12.02.

**3-Propylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5c)** mp 67.6-68.5ºC; IR (KBr): 1495, 1451, 1256 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.06 (t, 3H, *J* = 7.5 Hz), 1.90 (sixtet, 2H, *J* = 7.5 Hz), 2.34 (s, 3H), 3.22 (t, 2H, *J* = 7.5 Hz), 7.12 (d, 2H, *J* = 7.5 Hz), 7.31-7.43 (m, 7H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 14.4, 21.3, 23.8, 28.8, 124.6, 125.2, 128.65, 128.70, 129.1, 129.2, 138.1, 140.2, 154.0, 155.0; $^{77}$Se NMR (75 MHz, $CDCl_3$): δ 234.1; MS (EI): *m/z* = 357 $[M]^+$; Anal. Calcd for $C_{18}H_{19}N_3Se$: C, 60.67; H, 5.37; N, 11.79. Found: C, 60.55; H, 5.58; N, 11.44.

**3-Isopropylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5d)** mp 91.4-92.5ºC; IR (KBr): 1494, 1433, 1252 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.59 (d, 3H, *J* = 6.9 Hz), 1.62 (d, 3H, *J* = 6.9 Hz), 2.35 (s, 3H), 3.91-4.01 (m, 1H), 7.12 (d, 2H, *J* = 7.5 Hz), 7.32-7.44 (m, 7H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 21.4, 24.6, 34.0, 124.6, 125.3, 128.7, 128.8, 129.2, 129.3, 138.1, 140.3, 154.0, 155.0; $^{77}$Se NMR (75 MHz, $CDCl_3$): δ 357.6; MS (EI): *m/z* = 357 $[M]^+$; Anal. Calcd for $C_{18}H_{19}N_3Se$: C, 60.67; H, 5.37; N, 11.79. Found: C, 60.46; H, 5.55; N, 11.59.

**3-Cyclohexylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5e)** mp 112.7-114.1ºC; IR (KBr): 1500, 1449, 1250 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.30-1.49 (m, 3H), 1.58-1.65 (m, 1H), 1.69-1.81 (m, 4H), 2.18-2.26 (m, 2H), 2.35 (s, 3H), 3.82-3.91 (m, 1H), 7.12 (d, 2H, *J* = 8.0 Hz), 7.33-7.44 (m, 7H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 21.4, 25.7, 26.6, 34.4, 43.1, 124.6, 125.3, 128.7, 128.8, 129.17, 129.24, 138.1, 140.2, 153.8, 155.0; MS (EI): *m/z* = 397 $[M]^+$; Anal. Calcd for $C_{21}H_{23}N_3Se$: C, 63.63; H, 5.85; N, 10.60. Found: C, 63.38; H, 6.01; N, 10.32.

**3-Benzylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5f)** mp 84.6-86.0ºC; IR (KBr): 1594, 1498, 1453, 1255 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.35 (s, 3H), 4.49 (s, 2H), 7.12 (d, 2H, *J* = 8.0 Hz), 7.19-7.46 (m, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 21.4, 30.1, 124.5, 125.3, 127.0, 128.5, 128.7, 128.8, 129.1, 129.2, 129.3, 138.1, 138.3, 140.4, 154.2, 155.1; $^{77}$Se NMR (75 MHz, $CDCl_3$): δ 307.9; MS (EI): *m/z* = 405 $[M]^+$; Anal. Calcd for $C_{22}H_{19}N_3Se$: C, 65.35; H, 4.74; N, 10.39. Found: C, 64.95; H, 4.99; N, 10.09.

**3-Allylseleno-1-phenyl-5-*p*-tolyl-1*H*-1,2,4-triazole (5g)** mp 102.2-103.7ºC; IR (KBr): 1496, 1450, 1256 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.88 (d, 2H, *J* = 7.5 Hz), 5.04 (d, 1H, *J* = 9.7 Hz), 5.24 (d, 1H, *J* = 16.6 Hz), 6.08-6.18 (m, 1H), 7.13 (d, 2H, *J* = 8.0 Hz), 7.32-7.44 (m, 7H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 21.4, 28.9, 117.4, 124.5, 125.3, 128.7, 128.8, 129.2, 129.3, 134.5, 138.1, 140.3, 153.6, 155.1; $^{77}$Se NMR (75 MHz, $CDCl_3$): δ 274.5; MS (EI): *m/z* = 355 $[M]^+$.

**3-Ethylseleno-2-phenyl-5-*p*-tolyl-2*H*-1,2,4-triazole (6)** mp 85.0-86.5ºC; IR (KBr): 1595, 1504, 1335 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): δ 1.58 (t, 3H, *J* = 7.5 Hz), 2.39 (s, 3H), 3.35 (q, 2H, *J* = 7.5 Hz), 7.25 (d, 2H, *J* = 8.0 Hz), 7.42 (t, 1H, *J* = 7.5 Hz), 7.50 (t, 2H, *J* = 7.5 Hz), 7.61 (d, 2H, *J* = 7.5 Hz), 8.06 (d, 2H,

$J$ = 8.0 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 15.6, 21.4, 23.1, 124.1, 126.3, 128.0, 128.6, 129.2, 129.3, 137.8, 139.2, 146.1, 163.1; $^{77}$Se NMR (75 MHz, $CDCl_3$): δ 290.7; MS (EI): $m/z$ = 343 $[M]^+$; Anal. Calcd for $C_{17}H_{17}N_3Se$: C, 59.65; H, 5.01; N, 12.28. Found: C, 59.49; H, 5.16; N, 11.91.

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