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# Selenium-Nitrogen Bond Cleavage in Selenazole Ring System with Grignard Reagent: A Convenient Synthesis of Unsymmetrically Substituted Selenides

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# Selenium–Nitrogen Bond Cleavage in Selenazole Ring System with Grignard Reagent: A Convenient Synthesis of Unsymmetrically Substituted Selenides

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**Abstract:** High reactivity of the selenenamide bond in selenazoles toward nucleophiles can be exploited for synthesis of other organoselenium compounds. It has been found that benzisoselenazol-3(2*H*)-ones and related selenaheterocycles with an Se-N moiety treated with Grignard reagent gave unsymmetrical aryl-aryl and aryl-alkyl selenides in moderate to good yields. This reaction has a synthetic value because it is highly selective and can be realized under mild conditions.

**Keywords:** Grignard reagents, heterocycles, selenenamides, selenides

The selenenamides with endocyclic selenium–nitrogen moiety, such as benzisoselenazol-3(2*H*)-ones **1**, 1,3,2-benzothiaselenazoles 1,1-dioxides **2**, and 1,3,2-benzodiselenazoles **3**, are heterocyclic compounds of rising interest. They have been reported as catalysts for hydroperoxide oxidation of various organic functional groups, biological response modifiers, gluthathione peroxidase mimetics, and promising anti-inflammatory drugs.[1–3] The published papers generally have been devoted to synthesis of these heterocyclic systems, but only a few of them were focused on reactivity of the selenazole ring, although it has been postulated that their biological action and chemical properties are connected with the

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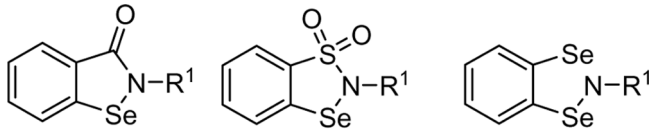
reactivity of selenenamide bond. As reported earlier, this bond was easily cleaved by treatment with nucleophilic reducing agents such as hydrazine, triphenylphosphine, and thiols.[4,5] The reactions with the carbon nucleophiles have been limited only to the treatment of 2-phenylbenzisoselenazol-3(2*H*)-one (ebselen) with buthyllithium to give 2-carbamoylphenylbutyl selenide.[6]

On the other hand, we focus our attention on diorganyl selenides because they are an important class of compounds employed as substrates and reagents in organic synthesis. Mainly, they are used for preparation of alkenes,[7] enones,[8] and epoxides[9] as well as aldehydes and ketones,[10] catalytic asymmetric imidation to selenimides,[11] and for synthesis of other organoselenium compounds.[12–14] Therefore, many methods of synthesis of selenides have been reported, but most of them involve multistep procedures or they require severe conditions and reagents of low stability.[15] During past years, the novel, mild procedures leading to selenides (e.g., the cross coupling reaction between diphenyl diselenides and alkyl halides promoted by equimolar amount of metallic lanthanum) were reported as alternative, one-pot syntheses of unsymmetric aryl-alkyl selenides.[16] Also, catalytic amounts of bimetallic zinc–indium(III) salts have been used to generate selenolate anions from diorganyl diselenides instead of lanthanum.[17] Preparation of selenides can be also carried out from diaryl diselenides and alkyl- and arylboronic acid using copper catalyst.[18] It noteworthy that all these methods employed diselenides as starting materials.

In this work, we report the reactions of benzisoselenazol-3(2*H*)-ones and their selenaheterocyclic analogs (Figure 1) with various alkyl- and arylmagnesium bromides as carbon nucleophiles. All the substrates used have a selenenamide moiety and other functional groups such as carbonyl group, sulfonyl group, and another selenium atom built in the heterocyclic ring. We found that interaction of nucleophilic carbon atom of Grignard reagent with a electrophilic center localized on a selenium atom




**1a** $R^1$ = Ph **2a** $R^1$ = *n*-Pr **3a** $R^1$ = *n*-Pr
**1b** $R^1$ = *n*-Pr **2b** $R^1$ = *t*-Bu **3b** $R^1$ = *t*-Bu

***Figure 1.***

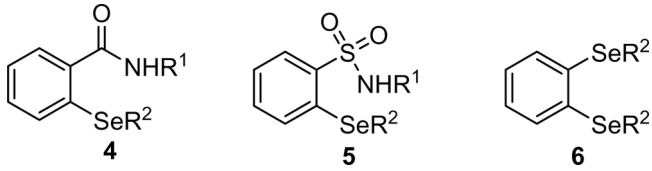


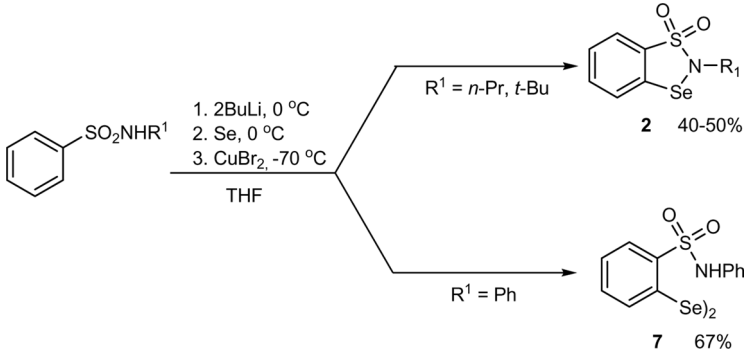

*Figure 2.*



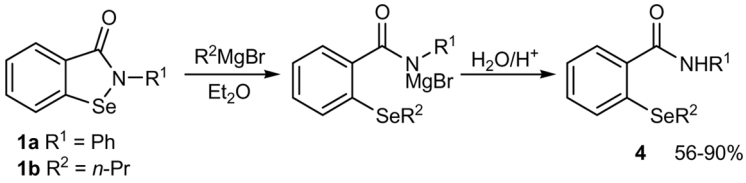
in selenenamides results in cleavage of Se-N bond and furnishes the corresponding diaryl or aryl-alkyl selenides **4**–**6** (Figure 2).

The key substrates, benzisoselenazol-3(2*H*)-ones **1**, were obtained from anthranilic acid in a four-step synthesis, the same way as reported earlier.[4,19] 1,3,2-Benzodiselenazoles **3** were prepared from *o*-diiodobenzene by selenenylation with lithium diselenide in hexamethylphosphoramide (HMPA) to poly(bis-1,2-phenylene) diselenide, which was converted into bis-1,2-(bromoseleno)benzene by treatment with bromine. Reaction of bis-1,2-(bromoseleno)benzene with aliphatic amines yields the corresponding 1,3,2-benzodiselenazoles **3**.[20]

The synthesis of 1,3,2-benzothiaselenazoles-1,1-dioxides **2** starting from *o*-sulfanilic acid in a seven-step process has been elaborated in our laboratory earlier.[21] In this work, we simplified the procedure and elaborated a new, one-pot method based on ortholithation of easily available benzenosulfonamides and reaction of 2-lithioderivatives with elementary selenium. After selenenylation, the formed intermediate was oxidatively cyclized with copper(II) bromide (Scheme 1). 1,3,2-Benzothiaselenazoles-1,1-dioxides **2** were isolated chromatographically in 40–50% yield. The residue was a tarry mixture of several compounds.




*Scheme 1.* Synthesis of 1,3,2-benzothiaselenazoles **2**.




***Scheme 2.*** Reaction of benzisoselenazol-3(2*H*)-ones **1**.



Nevertheless, the synthesis is limited only to N-alkyl-1,3,2-benzothiaselenazoles 1,1-dioxides. When N-phenylbenzenosulfonamide was a substrate, ring closure did not occur, and 2,2′-diselenobis(N-phenylbenzenosulfonamide) **7** was the only product.

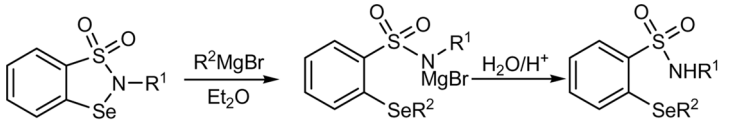
The model substrates taken for the reaction of selenenamide group with Grignard reagents were two benzisoselenazol-3(2*H*)-ones: 2-substituted with phenyl **1a** and *n*-propyl **1b**, two 2-alkyl-1,3,2-benzothiaselenazoles 1,1-dioxides **2a** ($R^1 = n$-propyl) and **2b** ($R^1 = t$-butyl), and two 2-alkyl-1,3,2-benzodiselenazoles **3a** ($R^1 = n$-propyl) and **3b** ($R^1 = t$-butyl). The Grignard reagents were prepared in the usual way from commercially available alkyl and aryl bromides such as bromobenzene, 3-bromoanisol, *n*-butyl bromide, and cyclohexyl bromide.

In the beginning, the reactions of **1** were carried out with equimolar amount of Grignard reagent (Scheme 2, Table 1, data given in brackets), but the products were accompanied by substantial amounts (about 40%) of starting benzizoselenazol-3(2*H*)-ones. The best results were obtained when alkyl- or arylmagnesium bromide was taken in 50% excess. Yields of pure selenides **4** were greater for all starting substrates. Only selenide

**Table 1.** Reaction of benzisoselenazol-3(2*H*)-ones **1** with alkyl or arylmagnesium bromides

| Substrate **1** | $R^1$ | $R^2$ | Product **4** | Yield (%) |
|---|---|---|---|---|
| **a** | $C_6H_5$ | $(CH_2)_3CH_3$ | **a** | 90 (63)[a] |
| | | $C_6H_5$ | **b** | 86 (55) |
| | | c-Hex | **c** | 56 (40) |
| | | 3-$CH_3OC_6H_4$ | **d** | 70 (49) |
| **b** | $(CH_2)_2CH_3$ | $(CH_2)_3CH_3$ | **e** | 89 (45) |
| | | $C_6H_5$ | **f** | 78 (56) |
| | | c-Hex | **g** | 81 (51) |
| | | 3-$CH_3OC_6H_4$ | **h** | 86 (60) |

[a]The yields of selenides **4** when substrates were used in 1:1 molar ratio.




***Scheme 3.*** Reaction of 1,3,2-benzothiaselenazoles 1,1-dioxides **2**.



**4c** was obtained in 56% yield, which could be caused by steric effect of two bulky (phenyl and cyclohexyl) groups bearing the substrate and reagent.

Reactivity of the selenenamide bond in 1,3,2-benzothiaselenazoles 1,1-dioxides **2** to Grignard reagents was similar to reactivity of this bond in benzisoselenazol-3(2*H*)-ones, and the reaction of **2** with alkyl- and aryl-magnesium bromides resulted in previously unknown alkyl-aryl and aryl-aryl selenides **5**, formed in good yields (Scheme 3, Table 2). Lesser yield of selenide **5g** was observed when the substrate and reagent have two bulky groups.

Similarly, 1,3,2-benzodiselenazoles **3** reacted with 2 equivalents of organomagnesium compound, but the yields were less than in previous cases (Table 3). The products were 1,2-di(alkylseleno)benzenes **6**, a new group of organoselenium compounds.

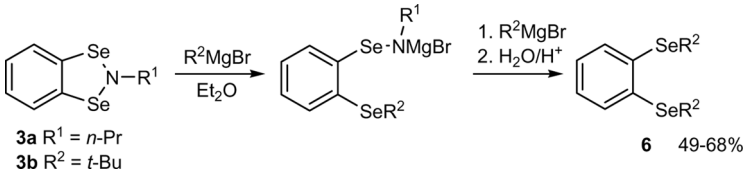
## EXPERIMENTAL

### General Methods

The reaction products were identified by their melting points (digital melting-points apparatus Electrothermal IA 911000), their $^1$H NMR data

**Table 2.** Reaction of 1,3,2-benzothiaselenazoles-1,1-dioxides **2** with alkyl or aryl-magnesium bromides

| Substrate **2** | $R^1$ | $R^2$ | Product **5** | Yield [%] |
|---|---|---|---|---|
| **a** | $(CH_2)_2CH_3$ | $(CH_2)_3CH_3$ | **a** | 60 |
| | | $C_6H_5$ | **b** | 84 |
| | | c-Hex | **c** | 75 |
| | | 3-$CH_3OC_6H_4$ | **d** | 73 |
| **b** | $C(CH_3)_3$ | $(CH_2)_3CH_3$ | **e** | 82 |
| | | $C_6H_5$ | **f** | 80 |
| | | c-Hex | **g** | 54 |
| | | 3-$CH_3OC_6H_4$ | **h** | 61 |




***Scheme 4.*** Reaction of 1,3,2-benzodiselenazoles **3**.



(δ, ppm, $CDCl_3$, tetramethylsilane (TMS), Bruker DRX 300-MHz spectrometer), $^{77}Se$ NMR data (δ, ppm, dimethyl sulfoxide (DMSO)-$d_6$, $Me_2S$ as external $^{77}Se$ standard, Bruker Avance 600-MHz spectrometer), and infrared (IR) spectra (Perkin-Elmer 2000FT spectrometer. Substrates, solvents, thin-layer chromatography (TLC) plates and silica gel for column chromatography (70–230 mesh) were purchased from Aldrich and Fluka.

Benzisoselenazol-3(2*H*)-ones **1** and 1,3,2-benzodiselenazoles **3** were prepared according to known procedures.[4,19,20]

## 2-Alkyl-1,3,2-benzothiaselenazole-1,1-dioxide (2): General Procedure

N-Alkylbenzenesulfonamide (10 mmol) was dissolved in 50 ml of dry tetra hydro furan (THF), and flask was immersed in an ice bath. After cooling, 14.4 ml of n-butyllithium (23 mmol, 1.6 M hexane solution) was added dropwise under nitrogen during 20 min, and the mixture was stirred for an additional 30 min. Then the selenium powder (0.79 g, 10 mmol) was added to the clear, yellow mixture in one portion. The reaction

**Table 3.** Reaction of 1,3,2-benzodiselenazoles **3** with alkyl or arylmagnesium bromides

| Substrate **3** | $R^1$ | $R^2$ | Product **6** | Yield (%) |
|---|---|---|---|---|
| **a** | $(CH_2)_2CH_3$ | $(CH_2)_3CH_3$ | **a** | 54 |
| | | $C_6H_5$ | **b** | 57 |
| | | c-Hex | **c** | 68 |
| | | 3-$CH_3OC_6H_4$ | **d** | 58 |
| **b** | $C(CH_3)_3$ | *n*-$(CH_2)_3CH_3$ | **e** | 50 |
| | | $C_6H_5$ | **f** | 58 |
| | | c-Hex | **g** | 49 |
| | | 3-$CH_3OC_6H_4$ | **h** | 62 |

mixture was stirred until selenium dissolved. After 2 h, the resulting dark red solution was cooled to −70°C, and copper(II) bromide (4.46 g, 20 mmol) was added. The mixture was kept at −70°C for 1 h, then cooling bath was removed and the flask was allowed to reach room temperature. Stirring continued for an additional 2 h, and then the mixture was poured into saturated aqueous solution of ammonium chloride (100 ml). The product was extracted with dichloromethane (DCM 3 × 50 ml), dried ($MgSO_4$), and evaporated. From the residue, pure 2-alkyl-1,3,2-benzothaselenazole-1,1-dioxide was isolated by column chromatography on silica gel using DCM as an eluent, yielding a proper product, which was recrystallized from carbon tetrachloride. 2-Propyl-1,3,2-benzothiaselenazole-1,1-dioxide **(2a)**: colorless crystals, yield 1.19 g (43%), mp 83–85°C (ref. 84–86°C[21]). 2-*tert*-Butyl-1,3,2-benzothiaselenazole 1,1-dioxide **(2b)**: colorless needles, yield 1.6 g (55%), mp 110–112°C (ref. 112–115°C[21]).



## Reaction of Selenenamides (1–3) with Grignard Reagents: General Procedure

The solution of Grignard reagent (prepared from 1.5 mmol or 3.0 mmol in case of **3** alkyl or aryl bromide and 1.5 mmol or 3.0 mmol in case of **3** magnesium turnings) in dry diethyl ether (5 ml) was cooled on an ice bath and stirred. The solution of selenenamide (1.0 mmol) in dry diethyl ether or tetrahydrofuran (THF, 10 ml) was added dropise. White precipitation appeared immediately. The mixture was refluxed for 2 h and then poured into water (30 ml). Selenide was extracted with methylene chloride (3 × 10 ml), purified by column chromatography on silica gel using $CH_2Cl_2$ for **4** and **5** or $CH_2Cl_2$–hexane 1:1 for **6** as an eluent, and recrystallized from chloroform–hexane.

## Data

2-(Butylselanyl)-*N*-phenylbenzamide (**4a**)

Yellow flakes, yield 0.28 g (90%), mp 93–94°C; $^1$H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, $J = 7.2$ Hz, $CH_3$), 1.40 (sext, 2H, $J = 7.5$ Hz, $CH_2$), 1.41–1.69 (m, 2H, $CH_2$), 2.92 (t, 2H, $J = 7.4$ Hz, $CH_2$), 7.14 (t, 1H, $J = 6.2$ Hz, ArH), 7.30–7.39 (m, 5H, ArH), 7.55–7.56 (m, 3H, ArH), 8.21 (s, 1H, NH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 301; IR (KBr): 3313, 2961, 1598, 737 cm$^{-1}$. Anal. calcd. for $C_{17}H_{19}NOSe$ (332.30): C, 61.45; H, 5.76; N, 4.22. Found: C, 61.44; H, 5.70; N 4.16.

2-(Phenylselanyl)-*N*-phenylbenzamide (**4b**)

Colorless flakes, yield 0.30 g (86%), mp 139–141°C; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.17–7.20 (m, 2H, ArH), 7.36–7.40 (m, 6H, ArH), 7.60–7.64 (m, 5H, ArH), 7.67–7.70 (m, 1H, ArH), 7.85 (s, 1H, NH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 447; IR (KBr): 3326, 3045, 1641, 1522, 751 cm$^{-1}$. Anal. calcd. for $C_{19}H_{15}NOSe$ (352.29): C, 64.78; H, 4.29; N, 3.98. Found: C, 64.70; H, 4.28; N, 3.95.

2-(Cyclohexylselanyl)-*N*-phenylbenzamide (**4c**)

Yield 0.18 g (52%), colorless powder, mp 100–102 C; $^1$H NMR (300 MHz, $CDCl_3$): δ 1.25–1.28 (m, 4H, $2CH_2$), 1.45–1.59 (m, 4H, $2CH_2$), 1.69–1.72 (m, 2H, $CH_2$), 1.95–1.99 (m, 2H, $CH_2$), 3.30–3.37 (m, 1H, CH), 7.15 (t, 1H, $J = 7.42$ Hz, ArH), 7.35–7.40 (m, 4H, ArH), 7.66 (d, 3H, $J = 8.8$ Hz, ArH), 7.83–7.86 (m, 1H, ArH), 8.69 (br, 1H, NH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 452; IR (KBr): 3275, 2924, 1641, 1598, 1321, 749 cm$^{-1}$. Anal. calcd. for $C_{19}H_{21}NOSe$ (358.34): C, 63.68; H, 5.91; N, 3.91. Found: C, 63.61; H, 5.86; N, 3.88.

2-(3-Methoxyphenylselanyl)-*N*-phenylbenzamide (**4d**)

Colorless plates, yield 0.26 g (70%), mp 122–123 C; $^1$H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H, $CH_3$), 6.91 (dd, 1H, $J = 8.06$ and $J = 2.57$ Hz, ArH), 7.13–7.16 (m, 3H, ArH), 7.22–7.29 (m, 5H, ArH), 7.37 (t, 2H, $J = 7.93$ Hz, ArH), 7.59 (d, 2H, $J = 7.82$ Hz, ArH), 7.65–7.68 (m, 1H, ArH), 7.82 (s, 1H, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 454; IR (KBr): 3306, 3065, 2955, 1622, 1586, 1243, 745 cm$^{-1}$. Anal. calcd. for $C_{19}H_{21}NOSe$ (358.34): C, 63.68; H, 5.91; N, 3.91. Found: C, 63.64; H, 5.89; N, 3.88.

2-(Butylselanyl)-*N*-propylbenzamide (**4e**)

Colorless powder, yield 0.25 g (85%), mp 48–50°C; $^1$H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, 3H, $J = 7.3$ Hz, $CH_3$), 1.00 (t, 3H, $J = 4.35$ Hz, $CH_3$), 1.44 (sext, 2H, $J = 7.2$ Hz, $CH_2$), 1.64 [m, 4H, $(CH_2)_2$], 2.89 (t, 2H, $J = 7.6$ Hz, $CH_2$), 3.42 (d, 2H, $J = 7.2$ Hz, $CH_2$), 6.28 (br, 1H, NH), 7.24–7.28 (m, 2H, ArH), 7.45–7.50 (m, 2H, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 301; IR (KBr): 3306, 2960, 1635, 1537, 739 cm$^{-1}$. Anal. calcd. for $C_{14}H_{21}NOSe$ (298.28): C, 56.31; H, 7.10; N, 4.70. Found: C, 56.24; H, 7.00; N, 4,75.

2-(Phenylselanyl)-*N*-propylbenzamide (**4f**)

Pale yellow needles, yield 0.25 g (85%), mp 78–79°C; $^1$H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, 3H, $J = 7.4$ Hz, $CH_3$), 1.62 (sext. 2H, $J = 7.3$ Hz, $CH_2$), 3.40 (q, 2H, $J = 7.3$ Hz, $CH_2$), 6.34 (br, 1H, NH), 7.05–7.07 (m, 1H, ArH), 7.12–7.15 (m, 2H, ArH), 7.34–7.36 (m, 3H, ArH), 7.48–7.50 (m, 1H, ArH), 7.61 (dd, 2H, $J = 5.4$ and $J = 1.5$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 449; IR (KBr): 3310, 2957, 1627, 1530, 744 cm$^{-1}$. Anal. calcd. for $C_{16}H_{17}NOSe$ (318.27): C, 60.38; H, 5.38; N, 4.40. Found: C, 60.40; H, 5.30; N, 4.35.

2-(Cyclohexylselanyl)-*N*-propylbenzamide (**4g**)

Light brown powder, yield 0.26 g (81%), mp 104–106°C; $^1$H NMR (300 MHz, $CDCl_3$): δ 1.02 (t, 3H, $J = 7.41$ Hz, $CH_3$), 1.25–1.39 (m, 2H, $CH_2$), 1.45–1.76 (m, 8H, $CH_2$), 2.00 (dd, 2H, $J = 12.97$ and $J = 2.26$ Hz, $CH_2$), 3.33 (tt, 1H, $J = 10.63$ and $J = 3.67$ Hz, CH), 3.43 (dd, 2H, $J = 13.28$ and $J = 6.77$ Hz, $CH_2$), 6.59 (s, 1H, NH), 7.28–7.33 (m, 2H, ArH), 7.59 (dd, 1H, $J = 5.89$ and $J = 3.20$, ArH), 7.63 (dd, 1H, $J = 5.54$ and $J = 3.76$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 351; IR (KBr): 3277, 3078, 2926, 1627, 1549, 688 cm$^{-1}$. Anal. calcd. for $C_{16}H_{23}NOSe$ (324.32): C, 59.25; H, 7.15; N, 4.32. Found: C, 59.19; H, 7.12; N, 4.28.

2-(3-Methoxyphenylselanyl)-*N*-propylbenzamide (**4h**)

Brown powder, yield 0.30 g (86%), mp 119–120°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, 3H, $J = 7.41$ Hz, $CH_3$), 1.58–1.70 (m, 2H, $CH_2$), 3.43 (t, 2H, $J = 7.14$ Hz, $CH_2$), 3.79 (s, 3H, $OCH_3$), 6.12 (s, 1H, NH), 6.91 (ddd, 1H, $J = 8.09$ and $J = 2.56$ and $J = 1.23$ Hz, ArH), 7.11–7.21 (m, 5H, ArH), 7.26 (t, 1H, $J = 3.93$ Hz, ArH), 7.50 (dd, 1H, $J = 5.66$ and $J = 3.43$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 436; IR (KBr): 3310, 2958, 1629, 1535, 1249, 742 cm$^{-1}$. Anal. calcd. for $C_{17}H_{19}NO_2Se$ (348.30): C, 58.62; H, 5.50; N, 4.02. Found: C, 58.57; H, 5.44; N, 3.99.

2-(Butylselanyl)-*N*-propylbenzenesulfonamide (**5a**)

Yellow oil, yield 0.20 g (60%). $^1$H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, 3H, $J = 7.41$ Hz, $CH_3$), 0.96 (t, 3H, $J = 7.37$ Hz, $CH_3$), 1.46–1.52 (m, 4H, $CH_2$), 1.74 (td, 2H, $J = 15.07$ and $J = 7.49$ Hz, $CH_2$), 2.83 (dd, 2H, $J = 13.56$ and $J = 6.85$ Hz, $CH_2$), 3.04–3.06 (m, 2H, $NCH_2$), 5.64 (t, 1H,

$J = 6.02$ Hz, NH), 7.37 (t, 1H, $J = 7.60$ Hz, ArH), 7.47 (t, 1H, $J = 7.60$ Hz, ArH), 7.63 (d, 1H, $J = 7.74$ Hz, ArH), 8.06 (d, 1H, $J = 7.83$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 305. IR (film): 3302, 3058, 2961, 2932, 1445, 1330, 1162, 757 $cm^{-1}$. Anal. calcd. for $C_{13}H_{21}NO_2SSe$ (334.34): C, 46.70; H, 6.33; N, 4.19; S, 9.59. Found: C, 46.67; H, 6.33; N, 4.18; S, 9.60.

2-(Phenylselanyl)-*N*-propylbenzenesulfonamide (**5b**)

Yellow oil, yield 0.29 g (84%). $^1$H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, 3H, $J = 7.40$ Hz, $CH_3$), 1.50–1.56 (m, 2H, $CH_2$), 2.94 (dd, 2H, $J = 13.49$ and $J = 6.82$ Hz, $CH_2$), 5.48 (t, 1H, $J = 6.01$ Hz, NH), 7.20 (dd, 1H, $J = 7.61$ and $J = 1.37$ Hz, ArH), 7.32 (ddd, 2H, $J = 9.67$ and $J = 7.53$ and $J = 1.54$ Hz, ArH), 7.42 (t, 2H, $J = 7.31$ Hz, ArH), 7.46 (t, 1H, $J = 7.30$ Hz, ArH), 7.62 (d, 2H, $J = 6.94$ Hz, ArH), 8.05 (dd, 1H, $J = 7.42$ and $J = 1.84$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 437; IR (film): 3310, 3058, 2965, 1443, 1327, 1161, 743 $cm^{-1}$. Anal. calcd. for $C_{15}H_{17}NO_2SSe$ (354.33): C, 50.85; H, 4.84; N, 3.95; S, 9.05. Found: C, 50.81; H, 4.80; N, 3.91; S, 9.01.

2-(Cyclohexylselanyl)-*N*-propylbenzenesulfonamide (**5c**)

Pale yellow oil, yield 0.27 g (75%). $^1$H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, 3H, $J = 7.32$ Hz, $CH_3$), 1.26–1.42 (m, 4H, $CH_2$), 1.45–1.58 (m, 6H, $CH_2$), 1.63–1.68 (m, 1H, CH), 2.03–2.08 (m, 2H, $CH_2$), 2.79 (q, 2H, $J = 6.79$ Hz, $CH_2$), 5.74 (t, 1H, $J = 6.43$ Hz, NH), 7.41 (m, 2H, ArH), 7.68 (d, 1H, $J = 7.56$ Hz, ArH), 8.07 (dd, 1H, $J = 7.79$ and $J = 1.60$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 400; IR (film): 3303, 2931, 1444, 1330, 1162, 757 $cm^{-1}$. Anal. calcd. for $C_{15}H_{23}NO_2SSe$ (360.37): C, 49.99; H, 6.43; N, 3.89; S, 8.90. Found: C, 49.89; H, 6.38; N, 3.87; S, 8.88.

2-(3-Methoxyphenylselanyl)-*N*-propylbenzenesulfonamide (**5d**)

Colorless oil, yield 0.28 g (73%). $^1$H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, 3H, $J = 7.40$ Hz, $CH_3$), 1.43–1.55 (m, 2H, $CH_2$), 2.91 (q, 2H, $J = 6.70$ Hz, $CH_2$), 3.82 (s, 3H, $OCH_3$), 5.45 (t, 1H, $J = 6.13$ Hz, NH), 6.97 (dd, 1H, $J = 8.39$ and $J = 2.75$ Hz, ArH), 7.16 (dd, 2H, $J = 7.83$ and $J = 0.98$ Hz, ArH), 7.21–7.25 (m, 1H, ArH), 7.30 (ddd, 3H, $J = 8.73$ and $J = 7.68$ and $J = 2.95$ Hz, ArH), 8.02 (dd, 1H, $J = 5.87$ and $J = 3.44$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 442; IR (film): 3311, 3060, 2965, 1587, 1161, 733 $cm^{-1}$. Anal. calcd. for $C_{16}H_{19}NO_3SSe$

(384.35): C, 50.00; H, 4.98; N, 3.64; S, 8.34. Found: C, 49.94; H, 4.96; N, 3.60; S, 8.30.

*N-tert*-Butyl-2-(butylselanyl)benzenesulfonamide (**5e**)

Colorless prisms, yield 0.27 g (82%), mp 81–82°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, 3H, $J = 7.4$ Hz, $CH_3$), 1.19 [s, 9H, $C(CH_3)_3$], 1.47 (q, 2H, $J = 7.4$ Hz, $CH_2$), 1.68–1.75 (m, 2H, $CH_2$), 3.03 (t, 2H, $J = 7.6$ Hz, $CH_2$), 5.63 (s, 1H, NH), 7.33 (t, 1H, $J = 1.22$ Hz, ArH), 7.41 (t, 1H, $J = 1.6$ Hz, ArH), 7.57 (dd, 1H, $J = 6.6$ and $J = 1.1$ Hz, ArH), 8.06 (dd, 1H, $J = 6.1$ and $J = 1.6$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 306; IR (KBr): 3245, 2966, 1311, 1147, 753 cm$^{-1}$. Anal. calcd. for $C_{14}H_{23}NO_2SSe$ (348.26): C, 48.27; H, 6.65; N, 4.02; S, 9.20. Found: C, 48.20; H, 6.59; N, 4.01; S, 9.18.

*N-tert*-Butyl-2-(phenylselanyl)benzenesulfonamide (**5f**)

Pale yellow prisms, yield 0.20 g (80%), mp 130–132°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 1.25 [s, 9H, $C(CH_3)_3$], 5.49 (s, 1H, NH), 7.18–7.20 (m, 1H, ArH), 7.26–7.29 (m, 2H, ArH), 7.38–7.42 (m, 3H, ArH), 7.60 (dd, 2H, $J = 5.9$ and $J = 1.6$ Hz, ArH), 8.04 (d, 2H, $J = 7$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 437. IR (KBr): 3310, 2933, 1326, 1154, 761 cm$^{-1}$. Anal. calcd. for $C_{16}H_{19}NO_2SSe$ (368.35): C, 52.17; H, 5.20; N, 3.80; S, 8.70. Found: C, 52.10; H, 5,15; N, 3,78; S, 8.62.

*N-tert*-Butyl-2-(cyclohexylselanyl)benzenesulfonamide (**5g**)

Pale yellow needles, yield 0.20 g (54%), mp 125–127°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 1.20 [s, 9H, $C(CH_3)_3$], 1.32–1.67 (m, 6H, $CH_2$), 1.75–1.81 (m, 2H, $CH_2$), 2.07 (dd, 2H, $J = 12.87$ and $J = 2.63$ Hz, $CH_2$), 3.57 (tt, 1H, $J = 10.76$ and $J = 3.70$ Hz, CH), 5.75 (s, 1H, NH), 7.32–7.43 (m, 2H, ArH), 7.65 (dd, 1H, $J = 7.44$ and $J = 1.55$ Hz, ArH), 8.09 (dd, 1H, $J = 7.60$ and $J = 1.78$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 425; IR (KBr): 3309, 3052, 2933, 1447, 1326, 1154, 761 cm$^{-1}$. Anal. calcd. for $C_{16}H_{25}NO_2SSe$ (374.40): C, 51.33; H, 6.73; N, 3.74; S, 8.56. Found: C, 51.30; H, 6.69; N, 3.70; S, 8.56.

*N-tert*-Butyl-2-(3-methoxyphenylselanyl)benzenesulfonamide (**5h**)

Colorless prisms, yield 0.24 g (61%), mp 134–136°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 1.24 [s, 9H, $C(CH_3)_3$], 3.80 (s, 3H, $OCH_3$), 5.46 (s, 1H, NH),

6.93–6.96 (m, 1H, ArH), 7.15 (d, 1H, $J = 1.57$ Hz, ArH), 7.18–7.19 (m, 1H, ArH), 7.23 (t, 1H, $J = 2.0$ Hz, ArH), 7.26–7.27 (m, 2H, ArH), 7.29–7.30 (m, 1H, ArH), 8.01–8.07 (m, 1H, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 442; IR (KBr): 3441, 3278, 2967, 1591, 1312, 1147, 759 $cm^{-1}$. Anal. calcd. for $C_{17}H_{21}NO_3SSe$ (398.38): C, 51.25; H, 5.31; N, 3.52; S, 8.05. Found: C, 51.22; H, 5.28; N, 3.28; S, 8.06.

1,2-Bis(butylselanyl)benzene (**6a, 6e**)

Orange oil, yield 0.2 g (57%). $^1$H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 6H, $J = 7.3$ Hz, $2CH_3$), 1.45 (q, 4H, $J = 7.6$ Hz, $2CH_2$), 1.66–7.76 (m, 4H, $2CH_2$), 2.87–2.98 (m, 4H, $2CH_2$), 7.08–7.16 (m, 2H, ArH), 7.49 (dd, 1H, $J = 5.8$ and $J = 1.6$ Hz, ArH), 7.61 (dd, 1H, $J = 7.7$ and $J = 1.6$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 284; IR (film): 3049, 2956, 2927, 1435, 745. Anal. calcd. for $C_{14}H_{22}Se_2$ (348.24): C, 48.28; H, 6.37. Found: C, 48.20; H, 6.20.

1,2-Bis(phenylselanyl)benzene (**6b, 6f**)

Yellow powder, yield 0.21 g (54%), mp 90–92°C. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.06–7.17 (m, 4H, ArH), 7.25–7.27 (m, 4H, ArH), 7.32–7.34 (m, 1H, ArH), 7.37–7.40 (m, 2H, ArH), 7.47 (dd, 1H, $J = 5.8$ and $J = 1.6$ Hz, ArH), 7.52 (m, 1H, ArH), 7.59 (dd, 1H, $J = 7.6$ and $J = 1.5$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 402; IR (KBr): 3057, 1433, 733 $cm^{-1}$. Anal. calcd. for $C_{18}H_{14}Se_2$ (388.22): C, 55.69; H, 3.36. Found: C, 55.58; H, 3.33.

1,2-Bis(cyclohexylselanyl)benzene (**6c, 6g**)

Yellow oil, yield 0.27 g (68%). $^1$H NMR (300 MHz, $CDCl_3$): δ 1.24–1.43 (m, 6H, $CH_2$), 1.57–1.65 (m, 6H, $CH_2$), 1.77–1.79 (m, 4H, $CH_2$), 2.04–2.10 (m, 4H, $CH_2$), 1.32–1.34 (m, 2H, CH), 7.03–7.09 (m, 1H, ArH), 7.13–7.16 (m, 1H, ArH), 7.52 (dd, 1H, $J = 7.44$ and $J = 1.48$ Hz, ArH), 7.63 (dd, 1H, $J = 7.78$ and $J = 1.42$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 419; IR (film): 3048, 2927, 2850, 1446, 743 $cm^{-1}$. Anal. calcd. for $C_{18}H_{26}Se_2$ (400.32): C, 54.01; H, 6.55. Found: C, 53.90; H, 6.49.

1,2-Bis(3-methoxyphenylselanyl)benzene (**6d, 6h**)

Yellow oil, yield 0.27 g (62%). $^1$H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 3H, $OCH_3$), 3.81 (s, 3H, $OCH_3$), 6.82 (dd, 1H, $J = 8.22$ and $J = 1.99$ Hz,

ArH), 6.89 (dd, 1H, $J = 8.22$ and $J = 2.00$ Hz, ArH), 6.96 (d, 1H, $J = 2.12$ Hz, ArH), 6.99 (d, 1H, $J = 7.71$ Hz, ArH), 7.13–7.16 (m, 2H, ArH), 7.21 (t, 2H, $J = 8.04$ Hz, ArH), 7.25–7.28 (m, 2H, ArH), 7.53 (dd, *1*H, $J = 7.56$ and $J = 1.29$ Hz, ArH), 7.65 (dd, 1H, $J = 7.90$ and $J = 1.10$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ 407. IR (film): 3050, 3000, 2934, 1562, 1435, 1038, 748 $cm^{-1}$. Anal. calcd. for $C_{20}H_{18}O_2Se_2$ (448.28): C, 53.59; H, 4.05. Found: C, 53.48; H, 3.99.



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