

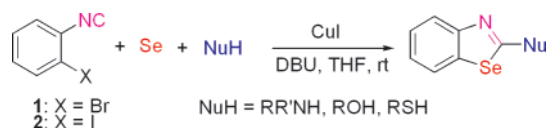
Copper(I)-Catalyzed Highly Efficient Synthesis of Benzoselenazoles and Benzotellurazoles

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A simple and practical useful synthetic method of 1,3-benzoselenazoles having a heteroatom substituent such as NRR' , OR, and SR groups at the 2-position was developed by the copper(I)-catalyzed reaction of 2-bromophenyl (1) or 2-iodophenyl (2) isocyanides with selenium and heteroatom nucleophiles. In addition, the synthesis of 2-amino-1,3-benzotellurazoles is also described.

Recently 1,3-benzothiazoles have attracted much attention not only in synthetic chemistry but also in medicinal and industrial fields. The benzothiazole ring is an important framework of pharmacologically active compounds,¹ cyanine dyes,² and

fluorescent³ and photochromic⁴ compounds. Therefore, diverse synthetic methods have been developed.^{5,6}

As for the selenium analogues, many selenium-containing heterocycles⁷ including nonfused 1,3-selenazoles^{8,9} possess biological activities and some 1,3-benzoselenazole derivatives are utilized as cyanine dyes.² Thus, 1,3-benzoselenazoles are expected to have promising importance, but the chemistry of benzoselenazole still remains much less explored in comparison to that of benzothiazole. This may be attributed to the lack of convenient and practical methods for the synthesis of 2-substituted benzoselenazoles.¹⁰ For example, the most commonly employed approach to the construction of the benzoselenazole ring may be the reaction of zinc bis(*o*-aminophenylselenoate) with acid chlorides;¹¹ however, this method cannot be applied to the synthesis of the 2-heteroatom-substituted benzoselenazoles. Here we describe a highly efficient method for the

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








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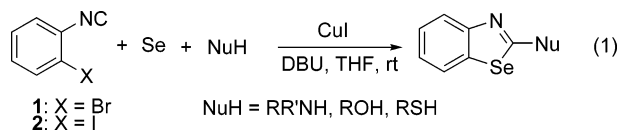
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TABLE 1. Synthesis of 2-Amino-1,3-benzoselenazoles^a

run	1 or 2	NuH	time	product	yield ^b
1	1		12 h		99%
2	1	Et ₂ NH	12 h		99%
3	1	ⁱ Pr ₂ NH	12 h		99%
4	1	EtPhNH	12 h		97%
5	1	BuNH ₂	12 h		0%
6	2		30 min	3a	99%
7	2	BuNH ₂	37 h	3e	71%
8	2		15 h		97%

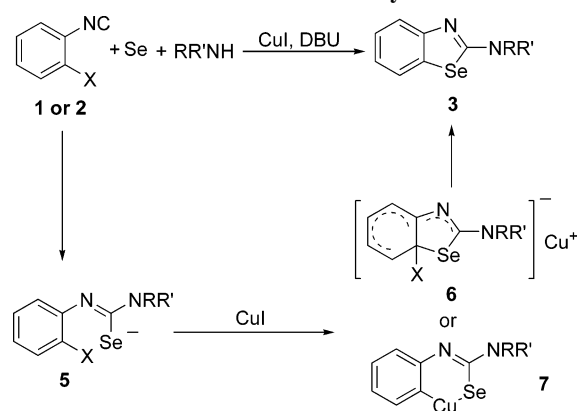
^a Reagents and conditions: **1** or **2** (1.0 mmol), Se (1.0 mmol), amine (1.2 mmol), DBU (1.0 mmol), CuI (1 mol %), THF (3 mL), rt, time shown in the table. ^b Isolated yield.

synthesis of 1,3-benzoselenazoles having a heteroatom substituent such as NRR', OR, and SR groups at the 2-position by the copper(I)-catalyzed reaction of 2-bromophenyl (**1**) or 2-iodophenyl (**2**) isocyanides with selenium and heteroatom nucleophiles (eq 1). In addition, conversion of prepared 2-arythio-1,3-benzoselenazole to 2-phenyl-1,3-benzoselenazole and the synthesis of 2-amino-1,3-benzotellurazoles are also described.



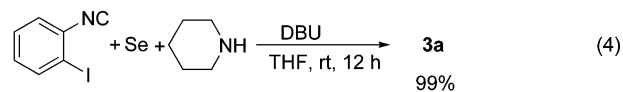
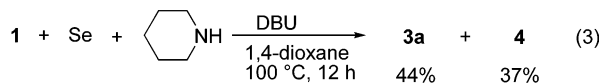
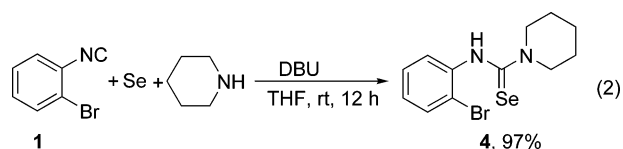
When piperidine (1.2 mmol) was allowed to react with selenium (1.0 mmol) and 2-bromophenyl isocyanide **1** (1.1 mmol) in THF (3 mL) in the presence of DBU (1.0 mmol) and 1 mol % of CuI at room temperature for 12 h, the corresponding 2-amino-1,3-benzoselenazole **3a** was formed in 99% isolated yield (Table 1, run 1). The results obtained by using several amines are summarized in Table 1. The present transformation proceeded almost quantitatively when aliphatic and aromatic secondary amines were used (runs 2–4), whereas when butylamine as a primary amine was employed, the corresponding product **3e** was not obtained at all (run 5). The reaction took place and proceeded very rapidly when 2-iodophenyl isocyanide (**2**) was employed instead of **1**. For example, **3a** was obtained quantitatively within 30 min (run 6). It is also notable that even when butylamine was employed, the product **3e** was obtained

SCHEME 1. Possible Reaction Pathway



in 71% yield although prolonged reaction time was needed (run 7). Imidazole also gave benzoselenazole **3f** in excellent yield (run 8).

To shed light on the mechanism we performed the following experiments. At first, **1** was allowed to react with piperidine and selenium without CuI under the same conditions as run 1. After aqueous workup, selenourea **4** was obtained in 97% yield; however, **3a** was not detected at all (eq 2).¹² Then we conducted the same reaction in 1,4-dioxane at 100 °C for 12 h and found that **3a** was formed in 44% yield along with 37% yield of **4** (eq 3). When **2** was employed instead of **1** in THF, **3a** was obtained in 99% yield without CuI at room temperature after 12 h (eq 4).



These results suggest that selenolate **5** in Scheme 1 is a precursor of benzoselenazole **3** and CuI accelerates cyclization of selenolate **5** to form **3**. Thus, we propose a reaction pathway including the S_NAr mechanism shown in Scheme 1.¹³ The first step of the process is selenoimidoylation of amines with selenium and isocyanides **1** or **2** yielding selenolates **5**. Subsequent intramolecular nucleophilic aromatic substitution via **6** affords selenazoles **3**. The role of CuI is not clear, but Cu(I)⁺ may stabilize intermediate complex **6** and/or facilitate elimination of the halogen atom from **6**. The copper-catalyzed cross-

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(13) The radical cyclization mechanism may be ruled out since when we performed the reaction in the presence of TEMPO, radical scavenger, no radical species were trapped with TEMPO and **3a** was formed quantitatively.

TABLE 2. Synthesis of 2-Substituted-1,3-benzoselenazoles^d

run	RYH	time	product	yield ^b
1 ^c	BuOH	12 h		83%
2 ^c	BnOH	12 h		87%
3 ^d	X = Me	12 h	8c : X = Me	89%
4	X = OMe	12 h	8d : X = OMe	98%
5 ^d	X = CO ₂ Me	35 h	8e : X = CO ₂ Me	48%
6	X = Me	2 h	9a : X = Me	98%
7	X = OMe	1 h	9b : X = OMe	96%
8	X = Cl	1 h	9c : X = Cl	93%
9	ⁿ C ₁₂ H ₂₅ SH	1 h	9d : S ⁿ C ₁₂ H ₂₅	92%

^a Reagents and conditions: **2** (1.0 mmol), Se (1.0 mmol), RYH (1.2 mmol), DBU (1.0 mmol), CuI (1 mol %), THF (3 mL), rt, time shown in the table. ^b Isolated yield. ^c CuI (2 mol %). ^d ROH (2.0 mmol).

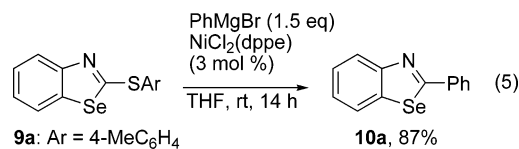
coupling reaction through oxidative addition intermediate **7** may also be possible.¹⁴

Reactions of alcohols with **2** and selenium were then examined since there is no example of the synthesis of 2-oxy-1,3-benzoselenazoles. Aliphatic alcohols and aromatic alcohols with an electron-donating substituent at the para position in the phenyl ring gave the desired products in high yields (Table 2, runs 1–4). When a carbomethoxy group was introduced at the para position, the reaction was slow and benzoselenazole **8e** was obtained only in 48% yield even by prolonging the reaction time to 35 h (run 5). Reactions of thiols, either aromatic or aliphatic, proceeded smoothly to give the corresponding products **9** in very high yields (runs 6–9).

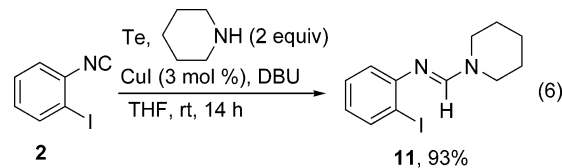
The coupling reaction of thus-formed 2-arylthio-1,3-benzoselenazole **9a** with PhMgBr was carried out aiming at the conversion to 2-phenyl-1,3-benzoselenazole. Treatment of **9a** with 1.5 equiv of PhMgBr in the presence of 3 mol % of NiCl₂(dppe)¹⁵ at room temperature for 14 h resulted in the formation of 2-phenyl-1,3-benzoselenazole **10a** in high yield (eq 5).¹⁶

Then, we attempted the construction of 1,3-benzotellurazoles rings¹⁷ since some 2-thio- and 2-amino-1,3-benzotellurazoles are reported to be utilized as photographic fog inhibitors.¹⁸ Our first trial employing tellurium under similar reaction conditions

(14) The oxidative addition mechanism was proposed in 2-aminothiazole synthesis by copper- and palladium-catalyzed intramolecular coupling reaction of *o*-haloarylthioureas, see ref 5e.



for 2-amino-1,3-benzoselenazoles failed, resulting in the formation of adduct **11** of piperidine onto isocyanide **2** (eq 6).



Since we already developed tellurium-assisted carbonylation¹⁹ and imidoylation²⁰ of amines with carbon monoxide and isocyanides, respectively, starting from lithium amides, we examined the reaction using lithium amides instead of amines. Lithium piperidide, generated from piperidine and *n*-BuLi in the presence of HMPA at –78 °C, was allowed to react with tellurium and then isocyanide **2** and CuI (5 mol %) were added at room temperature. 1,3-Benzotellurazole **12a** was obtained in 75% yield in 12 h (Table 3, run 1).²¹ Results employing other secondary amines are summarized in Table 3. In contrast to 1,3-benzoselenazole synthesis, this reaction was affected by bulkier substituents on the nitrogen of amines employed. For example, when diethylamine was used, **12b** was formed only in 31% yield (run 2) and diisopropylamine did not give benzotellurazole. Aromatic secondary amines such as ethyl phenylamine and diphenylamine afforded the expected products in moderate yields (runs 3 and 4).

In summary, we have developed simple and practical useful methods for the synthesis of 1,3-benzoselenazoles and 1,3-benzotellurazoles having heteroatom functionality at the 2-position. Since only a few classical preparative methods are available for such compounds,²² the reactions described herein would provide new convenient routes to these chalcogen-containing heterocycles.

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
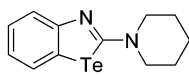
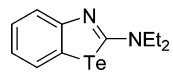
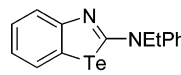
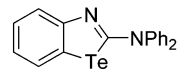
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(20) Maeda, H.; Matsuya, T.; Kambe, N.; Sonoda, N.; Fujiwara, S.; Shin-ike, T. *Tetrahedron* **1997**, *53*, 12159–12166.

(21) The present transformation is not affected by the amounts of CuI and additive very much. When the reactions were carried out by using 3 mol % of CuI or without HMPA, **12a** was obtained in 69% and 70% NMR yields, respectively.

(22) For 2-amino-1,3-benzoselenazoles, see: (a) Lok, R.; Leone, R. E.; Williams, A. J. *J. Org. Chem.* **1996**, *61*, 3289–3297. (b) Duddeck, H.; Bradenahl, R.; Stefaniak, L.; Jazwinski, J.; Kamienski, B. *Magn. Reson. Chem.* **2001**, *39*, 709–713. For 2-thio-1,3-benzoselenazoles: (c) Casar, Z.; Leban, I.; Maréchal, A. M.-L.; Lorczy, D. *J. Chem. Soc., Perkin Trans.* **2002**, *1*, 1568–1573. 2-Amino-1,3-tellurazoles were prepared by the reaction of TeCl₄ with aromatic ureas, see ref 18.

TABLE 3. Synthesis of 2-Amino-1,3-benzotellurazoles^a

$\text{RR'NH} \xrightarrow[\text{THF, } -78^\circ\text{C, 30 min}]{1) ^n\text{BuLi, HMPA}} \xrightarrow[\text{2, } \text{rt, 12 h}]{2) \text{Te, } -78^\circ\text{C, then rt, 1 h}} \text{Product } \mathbf{12}$			
run	RR'NH	product	yield ^b
1		 12a	75%
2	Et ₂ NH	 12b	31%
3	EtPhNH	 12c	53%
4	Ph ₂ NH	 12d	65%

^a Reagents and conditions: (1) RR'NH (1.2 mmol), ⁿBuLi (1.2 mmol), HMPA (3.0 mmol), THF (5 mL). (2) Te (1.0 mmol). (3) **2** (1.1 mmol), CuI (5 mol %). ^b Isolated yield.

Experimental Section

2-(1-Piperidyl)-1,3-benzoselenazole (3a): Typical Procedure for the Synthesis of 1,3-Benzoselenazoles. Into a flame-dried flask were added selenium (1.0 mmol), DBU (1.0 mmol), THF (3 mL), 2-bromophenyl isocyanide (**1**, 1.1 mmol), piperidine (1.2 mmol), and CuI (0.01 mmol) at room temperature, and the mixture was stirred for 12 h. The mixture was then poured into sat. NaHCO₃ aq and extracted with Et₂O. After the organic phase was dried over MgSO₄ and filtered, the filtrate was concentrated in vacuo and purified by silica gel column chromatography eluted with *n*-hexane–Et₂O (5/1) to give 2-(1-piperidyl)-1,3-benzoselenazole (**3a**)

as a red solid: mp 61.0–62.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.68 (br s, 6 H), 3.55 (br s, 4 H), 6.94–6.98 (m, 1 H), 7.24–7.28 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 24.3, 25.4, 50.8, 119.7, 120.8, 123.5 (¹*J*_{Se–C} = 8.1 Hz), 125.8, 133.0, 154.4, 168.8; IR (KBr) 2936, 1593, 1532, 1446, 752 cm⁻¹; MS (EI), *m/z* 266 (M⁺, 100). Anal. Calcd for C₁₂H₁₄N₂Se: C, 54.34; H, 5.32; N, 10.56. Found: C, 54.07; H, 5.17; N, 10.40.

2-(1-Piperidyl)-1,3-benzotellurazole (12a): Typical Procedure for the Synthesis of 2-Amino-1,3-benzotellurazole. *n*-BuLi (1.2 mmol) was added to a solution of piperidine (1.2 mmol), HMPA (3 mmol), and THF (5 mL) at –78 °C. After 30 min, tellurium (1.0 mmol) was added and the mixture was warmed to room temperature. 2-Iodophenyl isocyanide (**2**, 1.1 mmol) and CuI (0.05 mmol) were added at room temperature, and the mixture was stirred for 12 h. The mixture was then poured into sat. NaHCO₃ aq and extracted with Et₂O. After the organic phase was dried over MgSO₄ and filtered, the filtrate was concentrated in vacuo and purified by silica gel column chromatography eluted with *n*-hexane–Et₂O (5/1) to give 2-(1-piperidyl)-1,3-benzotellurazole **12a** as a white solid: mp 74.0–76.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.67 (br s, 6 H), 3.50 (br s, 4 H), 6.83–6.87 (m, 1 H), 7.23–7.27 (m, 1 H), 7.56–7.60 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 24.6, 25.6, 52.5, 120.6, 120.8, 126.7, 127.8, 130.3 (¹*J*_{Te–C} = 15.7 Hz), 159.8, 164.3; IR (KBr) 2931, 1515, 1436, 1199, 751 cm⁻¹; MS (EI), *m/z* 316 (M⁺, 74). Anal. Calcd for C₁₂H₁₄N₂Te: C, 45.92; H, 4.50; N, 8.93. Found: C, 45.75; H, 4.36; N, 8.81.

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Supporting Information Available: Characterization data and copies of ¹H and ¹³C NMR charts of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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