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Synthesis of Fully Functionalized 5-Selanyl-1,2,3-triazoles: Copper-Catalyzed Three-Component Reaction of Ethynylstibanes, Organic Azides, and Diaryl Diselenides

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Abstract

A simple general method for the synthesis of fully substituted 5-selanyl-1,2,3-triazoles is described. In the presence of CuI (10 mol%) and 1,10-phenanthroline (10 mol%), three-component reaction of ethynylstibanes, organic azides and diaryl diselenides afforded 5-selanyltriazoles in moderate-to-excellent yields. Under an aerobic conditions, the reaction proceeded efficiently in that two selanyl groups were transferred from the diaryl diselenide to the products. In this three-component reaction, ethynylstibanes having antimony atom gave superior results compared to various alkynes having other typical elements such as silicon, tin, and tellurium.

Key words: three-component reaction, 5-selanyl-1,2,3-triazole, ethynylstibane, organic azide, diaryl diselenide, copper catalyst

Introduction

Organoselenium compounds have garnered attention in various areas of science, such as biology and organic synthesis.[1,2] Among them, diaryl selenides have been of particular interest in the last two decades owing to their wide applicability in biological and pharmaceutical fields because of their anticancer, antitumor, antiviral, antimicrobial, and antioxidant activities.[3] Recently, interest in selenides having a heterocyclic ring is rising due to their biological activities. For instance, 4-arylselanyl-7-chloroquinolines act as potential antioxidants,[4] selenofonsartan analogues having imidazolyl group inhibit Angiotensin II type 1 (AT1) receptor,[5] and 3-(arylselanyl)selenophenes exhibit antidepressant-like properties.[6] Several methods have been developed for the synthesis of unsymmetrical diaryl selenides. Transition-metal-catalyzed C–Se bond formation is one of the most popular methods for the synthesis of organoselenides.[1c,7] Among them, diaryl diselenide is superior to other selenium reagents (selenol, arylselenium bromide, and alkyltin selenide) as the selanyl source for the synthesis of diaryl selenides in terms of odor, stability, and toxicity. For instance, it is known that Cu-catalyzed C(aryl)–Se bond formation by reacting diaryl diselenides with aryl halides,[8] aryl boronic acids,[9] and triarylbismuthanes[10] led to the formation of unsymmetrical diaryl selenides. Synthesis of fully functionalized 1,2,3-triazoles have drawn considerable interest because of their potential in medicinal chemistry and as pharmacophores of numerous bioactive compounds.[11] Among these, the synthesis of fully functionalized 1,2,3-triazoles having selenium atom as a substituent at the C-5 position was recently attempted using transition-metal-mediated azide-alkyne cycloaddition with high levels of regioselectivity. In 2009, Benhida et al. carried out the three-component reaction of terminal alkynes, ribosyl azides, and phenylselanyl bromide in the presence of CuI (1.2 eq) and *N,N*-diisopropylethylamine (3 eq).[12] In 2014, Sun et al. reported the cycloaddition of butylethynyl phenyl selenide with benzyl azide using iridium catalyst $[Ir(cod)Cl]_2$ (2 mol%).[13] In 2016, Xu et al. carried out the three-component reaction of a terminal alkyne, benzyl azide, and phenylselanyl benzenesulfonate ($PhSO_2SePh$) in the presence of CuI (20 mol%) and LiO^tBu (2 eq).[14] However, these reactions have low applicability of the 5-position selanyl group because the selenium reagents being used are not always commercially available and require complicated preparation steps.

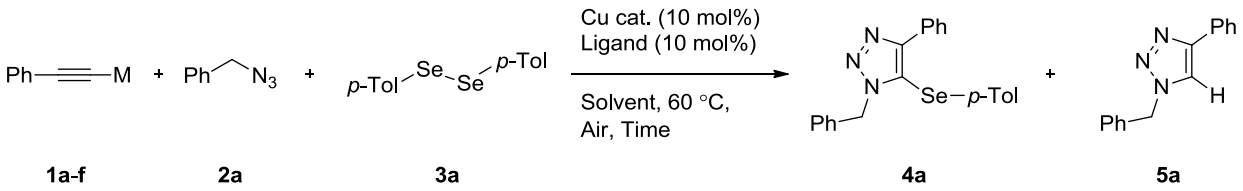
In 2016, Ackermann et al. reported an efficient and versatile method using Cu-catalyzed C–H selanylation of 1,4-disubstituted 1,2,3-triazoles with diaryl diselenides.[15] One drawback of this reaction is the requirement of an amide moiety at the C-4 position in triazoles for C–H activation. To the best of our knowledge, synthesis of fully functionalized 5-selanyl-1,2,3-triazoles using Cu-catalyzed C(aryl)–Se bond formation based on a selenium-induced reaction via exchange of typical elements has not been reported. Recently, we found that Cu-catalyzed azide-alkyne cycloaddition of ethynylstibanes with organic azides can be converted to fully substituted 5-organostibano-1,2,3-triazoles bearing antimony, [16] which could be employed as versatile building blocks in chemical synthesis.[17] As a follow up to our studies, we present here the synthesis of fully functionalized 5-selanyl-1,2,3-triazoles under aerobic conditions by Cu-catalyzed three-component reaction of ethynylstibanes, organic azides, and diaryl diselenides.

Results and Discussion

We initially focused our attention on the determination of optimal conditions for the synthesis of 5-selanyl-1,2,3-triazole **4a** using benzyl azide **2a**, di-*p*-tolyl diselenide **3a** and various alkynes **1** having typical elements such as Si, Sn, Sb, and Te. The results of the experiments to identify suitably active alkynes, catalysts, ligands, and solvents for the three-component reaction, are summarized in Table 1. The yield and reaction time for reaction of various alkynes **1a-d** (0.5 mmol), **2a** (0.5 mmol), and **3a** (0.25 mmol) under aerobic conditions in DMSO at 60 ºC using CuI (0.05 mmol) as catalyst and 1,10-phenanthroline (0.05 mmol) as ligand are given as entries 1-4 (Table 1). Ethynylstibane **1c** was found to be the best alkyne for the reaction in terms of the yield of the expected triazole **4a**, the reaction time, and the yield of byproduct **5a**. It should be emphasized that in the present three-component reaction, both the selanyl groups were transferred from diselenide to the coupling product **4a**. When copper acetylide **1e** was used instead of ethynylstibane **1c**, the reaction time prolonged and the yield decreased (entry 5). Additionally, ethynylbenzene **1f** was found inactive for this reaction (entry 6). Several available Cu catalysts were then screened for their suitability in the reaction of **1c** with **2a** and **3a** (entries 3, 7-15). CuI was the best catalyst for this reaction in terms of the yield (87%)

of **4a** and reaction time (3 h). Various ligands were screened next (entries 3, 16-24), among which 1,10-phenanthroline was the most effective. Screening of solvents showed that the reaction proceeded efficiently in DMSO (87%), DMF (69%), NMP (68%), and 1,2-DCE (63%), whereas CH_3CN, EtOH, THF, and toluene were inefficient reaction solvents (entries 3, 25-32). The reaction at room temperature required a long reaction time of 24 h (entry 33). When the reactions were performed under argon and oxygen, the product was obtained in a lower yields (entries 34 and 35). Results suggested that presence of oxygen and water in the air are necessary for the reaction. The reaction is easy to operate under aerobic conditions, which are thus considered excellent reaction conditions. Catalyst loading influenced the yield of products and the reaction time. Decreasing the loading of CuI from 10 mol% to 5 mol% and 1 mol% significantly reduced the yield of **4a** and reaction time prolonged (entries 36 and 37). The best result was obtained under aerobic conditions at 60 °C when **1c**, **2a**, and **3a** were treated with CuI and 1,10-phenanthroline in DMSO. The regiochemistry of 5-selanyltriazole **4a** was elucidated by ^{1}H NMR spectroscopy and confirmed by single-crystal X-ray analysis (Figure 1). A nuclear Overhauser effect (NOE) was observed between the benzylic protons and the aromatic protons of the *p*-tolyl group.

Table 1. Optimization of reaction conditions.[a]



1a-f **2a** **3a** **4a** **5a**

En.	M	Cu cat.	Ligand	Solvent	Time (h)	Yield (%)[b]	
						4a	**5a**
1	**1a**: $SiMe_3$	CuI	1,10-Phen.	DMSO	4	62	19
2	**1b**: $Sn(nBu)_3$	CuI	1,10-Phen.	DMSO	3	3	26
3	**1c**: $SbPh_2$	CuI	1,10-Phen.	DMSO	3	87	8
4	**1d**: Te*n*Bu	CuI	1,10-Phen.	DMSO	24	32	---
5	**1e**: Cu	CuI	1,10-Phen.	DMSO	24	61	---
6	**1f**: H	CuI	1,10-Phen.	DMSO	24	30	---
7	**1c**: $SbPh_2$	CuBr	1,10-Phen.	DMSO	3	65	25
8	**1c**: $SbPh_2$	CuCl	1,10-Phen.	DMSO	2	73	26
9	**1c**: $SbPh_2$	CuOAc	1,10-Phen.	DMSO	2	47	26
10	**1c**: $SbPh_2$	Cu_2O	1,10-Phen.	DMSO	4	58	35
11	**1c**: $SbPh_2$	$CuBr_2$	1,10-Phen.	DMSO	2	44	31
12	**1c**: $SbPh_2$	$Cu(OAc)_2$	1,10-Phen.	DMSO	3	23	38

13	**1c**: $SbPh_2$	CuO	1,10-Phen.	DMSO	24	30	<5
14	**1c**: $SbPh_2$	$CuSO_4$	1,10-Phen.	DMSO	4	47	50
15	**1c**: $SbPh_2$	---	1,10-Phen.	DMSO	23	25	28
16	**1c**: $SbPh_2$	CuI	PPh_3	DMSO	7	39	49
17	**1c**: $SbPh_2$	CuI	TEA	DMSO	2	26	69
18	**1c**: $SbPh_2$	CuI	Proline	DMSO	24	23	75
19	**1c**: $SbPh_2$	CuI	EDA	DMSO	23	56	28
20	**1c**: $SbPh_2$	CuI	2,2'-Bipyridyl	DMSO	2	81	17
21	**1c**: $SbPh_2$	CuI	DMEDA	DMSO	23	5	33
22	**1c**: $SbPh_2$	CuI	TMEDA	DMSO	4	48	46
23	**1c**: $SbPh_2$	CuI	PMDTA	DMSO	3	23	66
24	**1c**: $SbPh_2$	CuI	---	DMSO	3	42	57
25	**1c**: $SbPh_2$	CuI	1,10-Phen.	DMF	2	69	28
26	**1c**: $SbPh_2$	CuI	1,10-Phen.	NMP	4	68	31
27	**1c**: $SbPh_2$	CuI	1,10-Phen.	CH_3CN	4	46	14
28	**1c**: $SbPh_2$	CuI	1,10-Phen.	1,4-Dioxane	24	25	15
29	**1c**: $SbPh_2$	CuI	1,10-Phen.	EtOH	23	59	28
30	**1c**: $SbPh_2$	CuI	1,10-Phen.	THF	23	25	28
31	**1c**: $SbPh_2$	CuI	1,10-Phen.	DCE	3	63	34
32	**1c**: $SbPh_2$	CuI	1,10-Phen.	Toluene	24	25	13
33[c]	**1c**: $SbPh_2$	CuI	1,10-Phen.	DMSO	24	71	9
34[d]	**1c**: $SbPh_2$	CuI	1,10-Phen.	DMSO	24	37	26
35[e]	**1c**: $SbPh_2$	CuI	1,10-Phen.	DMSO	2	36	35
36	**1c**: $SbPh_2$	CuI (5%)	1,10-Phen. (5%)	DMSO	7	62	33
37	**1c**: $SbPh_2$	CuI (1%)	1,10-Phen. (1%)	DMSO	24	53	31

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), **3a** (0.25 mmol). [b] Isolated yield. [c] At room temperature. [d] Under argon. [e] Under O_2.

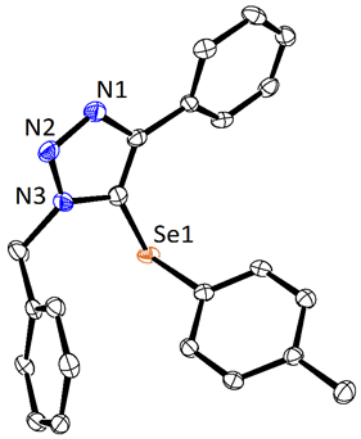


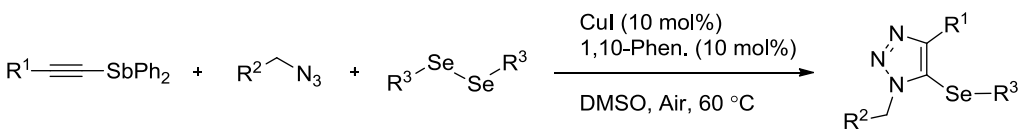
Figure 1. Ortep drawing of **4a** with 50% probability. All hydrogen atoms are omitted for clarity.

To demonstrate the efficiency and generality of this three-component reaction, the reactions of various ethynylstibanes (**1**: 0.5 mmol), organic azides (**2**: 0.5 mmol), and diaryl diselenides (**3**: 0.25 mmol) were investigated under aerobic conditions in DMSO using the catalytic system of CuI (10 mol%)

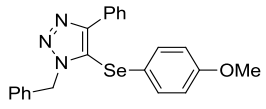
and 1,10-phenanthroline (10 mol%) at 60 °C. Ethynylstibanes **1** of the key starting material could be easily prepared according to the general method used previously.[18] The terminal alkynes were treated with *n*-BuLi in dry ether under an argon atmosphere at 0 °C, and followed by trapping with diphenylantimony bromide to afford arylethynyl, vinylethynyl, and alkylethynyl compounds in 44–83% yields. The results of three-component reaction are summarized in Table 2. Reactions of ethynylstibane **1c**, benzyl azide **2a**, and diaryl diselenides **3** gave the corresponding 5-selanyl-1,2,3-triazoles **4a-m** in good-to-excellent yields (60–98%), except for the benzyl selenide derivative **4n** (38%). For **4a-f**, the substituent on the benzene ring of diselenides did not affect the progress of the reaction. The reaction of sterically hindered *ortho*-substituted diselenides gave the corresponding selenides **4g-k** including CH_2NMe_2 and acetamide moieties without any difficulty. With diaryl diselenides having heterocyclic ring, this reaction gave **4l** and **4m**. Dibenzyl diselenide having benzyl moiety as the alkyl group resulted in lower yield of **4n** than diaryl diselenides. Various ethynylstibanes **1** were then reacted with benzyl azide **2a** and diphenyl diselenide under the same reaction conditions. Ethynylstibanes **1** with functional groups such as aryl, vinyl, and alkyl also afforded the corresponding products **4o-s** in satisfactory yields. The electronic nature of the substituents in **1** did not affect the outcome of the reaction. Furthermore, various organic azides **2** bearing cinnamyl, (ethoxycarbonyl)methyl, 1-naphthalenemethyl and (phenylthio)methyl groups were reacted with **1c** and diphenyl diselenide to afford the corresponding triazoles **4t-w** in moderate yields. However, the reaction with aryl-azides such as 4-methylphenyl- and 4-cyanophenyl-azide gave a complex mixture. We have recently reported that 5-stibanotriazoles could not be obtained in the Cu-catalyzed [3+2] cycloaddition of (phenylethynyl)di-*p*-tolylstibane with aryl-azides.[16] Even in the three-component reaction, there might be a problem with the cyclization step.

10.1002/ejoc.201701389

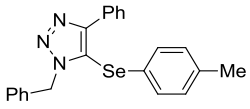
Table 2. Study of substrate scope[a,b]



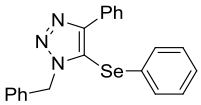
1c, g-k **2a-e** **3a-n** **4a-w**



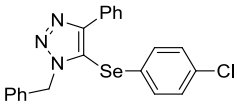
4b: 77% (3 h)



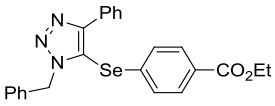
4a: 87% (3 h)



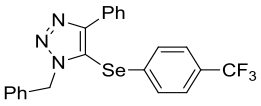
4c: 65% (2 h)



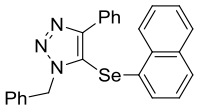
4d: 71% (3 h)



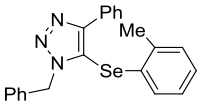
4e: 82% (3 h)



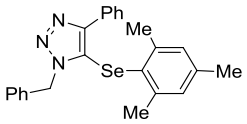
4f: 98% (3 h)



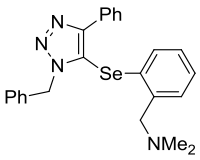
4g: 84% (4 h)



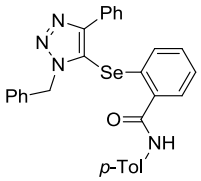
4h: 81% (3 h)



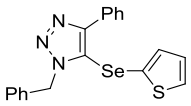
4i: 73% (2 h)



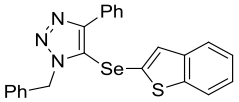
4j: 70% (1 h)



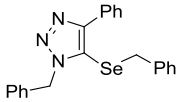
4k: 65% (2 h)



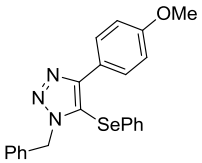
4l: 67% (1 h)



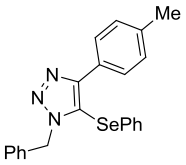
4m: 60% (2 h)



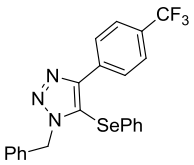
4n: 38% (2 h)



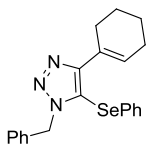
4o: 75% (4 h)



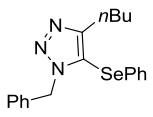
4p: 73% (3 h)



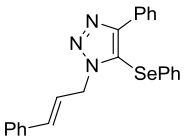
4q: 73% (1 h)



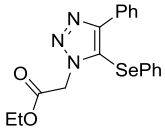
4r: 74% (2 h)



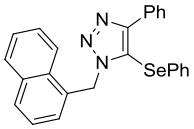
4s: 83% (2 h)



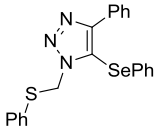
4t: 57% (2 h)



4u: 52% (4 h)



4v: 62% (3 h)

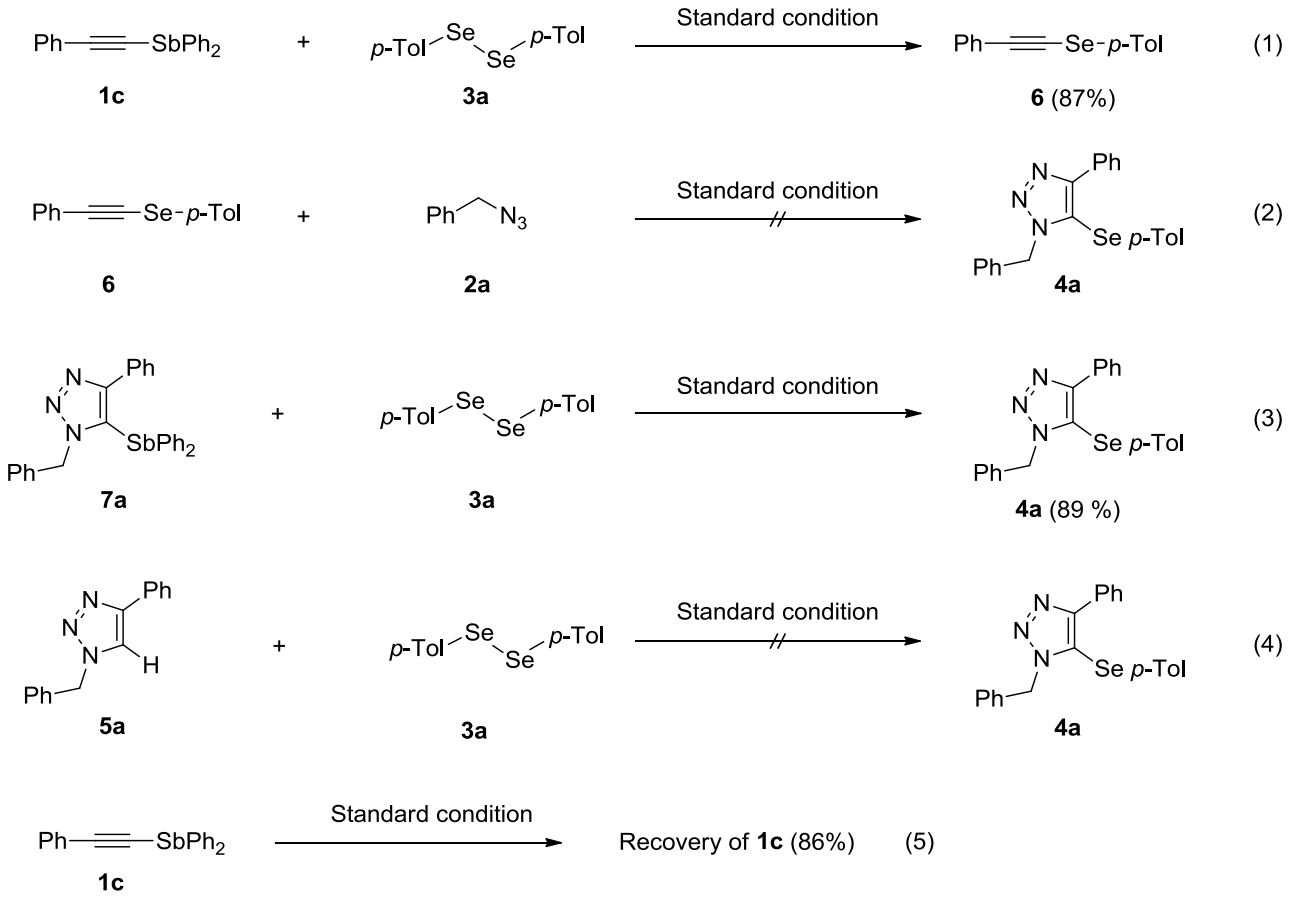


4w: 59% (2 h)

[a] **1** (0.5 mmol), **2** (0.5 mmol), **3** (0.25 mmol), CuI (0.05 mmol), 1,10-Phen. (0.05 mmol).

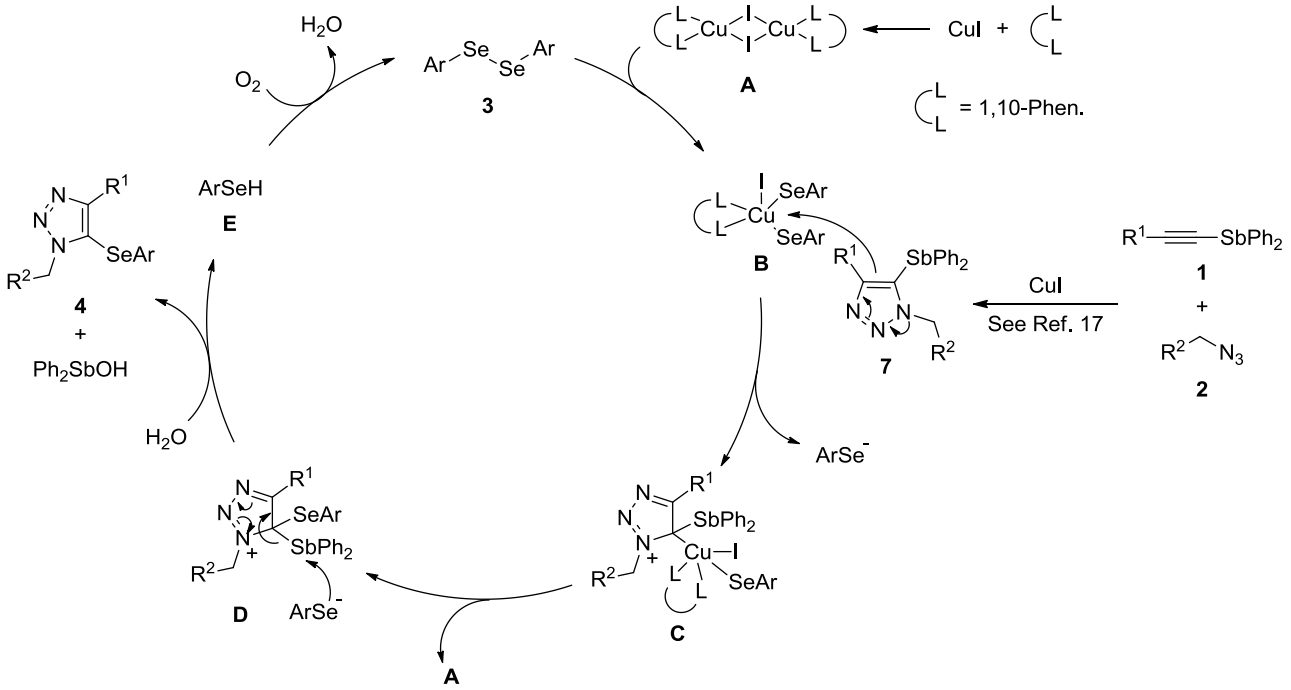
[b] Isolated yield.

A control experiment was conducted to propose a reaction mechanism. The reaction of ethynylstibane **1c** with di-*p*-tolyl diselenide **3a** under standard conditions afforded the ethynylselenide **6** in 87% yield (Eq. 1). However, the cycloaddition of **6** with benzyl azide **2a** did not progress (Eq. 2). The type of reaction might differ between three- and stepwise two-component reactions. For instance, Xu et al. reported Cu-catalyzed three-component reaction of terminal alkynes, benzyl azide, and benzenesulfonothioate for the synthesis of fully functionalized 5-sulfanyltriazoles.[14] The two-component reaction of phenylacetylene with benzenesulfonothioate afforded the ethynylsulfide in high yield. However, the reaction of ethynylsulfide and benzyl azide does not proceed. The reaction of 5-stibanotriazole **7a**[17a] with **3a** obtained the corresponding 5-selanyltriazole **4a** in high yield (Eq. 3). On the other hand, **4a** could not be produced by the reaction of **5a** with **3a** (Eq. 4). Heating of ethynylstibane **1c** without azide and diselenide under standard condition recovered **1c** at isolated yield 86% (Eq. 5). In this reaction, trace amounts of ethynylbenzene were observed in gas-liquid chromatography, while 1,4-diphenylbuta-1,3-diyne was not detected. Three-component reaction of **1c**, **2a**, and **3a** with 1 equivalent of TEMPO as radical scavenger gave 5-selanyltriazole **4a** in satisfactory yield (81%).



Scheme 1. Control experiments

Based on the above control experiments, a possible mechanism for this three-component reaction is shown in Scheme 2. This reaction involves the formation of 5-stibanotriazole **7** from ethynylstibane **1** and azide **2** in the presence of a Cu catalyst. [16,17b] Moreover, diaryl diselenide **3** reacts with bimetallic complex [(phen)$_2$CuI$_2$] **A** to generate Cu(III) intermediate **B**.[19] Compound **7** would attack the intermediate **B** at the 5-position on the triazole to form intermediate **C**, which undergoes reductive elimination to give the intermediate **D** with regeneration of the Cu complex. The aryl selenide anion attacks the antimony to generate 5-selanyltriazole **4** and Ph_2Sb–SeAr, which is hydrolyzed with H_2O in the air and converted to selenol **E** and Ph_2SbOH. Selenol **E** is converted to diselenide **3** by air oxidation. Therefore, the reaction proceeds with 0.5 equivalents of diselenide and two selanyl groups can be used for the reaction.



Scheme 2. Proposed mechanism

In conclusion, we developed simple Cu-catalyzed three-component reaction for the synthesis of fully substituted 5-selanyl-1,2,3-triazoles under aerobic conditions without the need for any additives. The reaction is atom-economic and both selanyl groups on the diaryl diselenide participated in the reaction. Ethynylstibanes, organic azides, and diselenides with different functional groups afforded the corresponding products with satisfactory yields. Detailed mechanistic studies of this three-component reaction and its application to medicinal chemistry are in progress and will be reported in the future.

Experimental Section

General Information

Melting points were measured on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and reported as uncorrected values. ^{1}H NMR (TMS: δ: 0.00 or CH_2Cl_2: 5.30 ppm as an internal standard) and ^{13}C NMR ($CDCl_3$: δ: 77.00 or DMSO-d_6: δ: 39.52 ppm as an internal standard) spectra were recorded on JEOL JNM-AL400 (400 MHz and 100 MHz) spectrometers in $CDCl_3$. Mass spectra were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 mA). IR spectra were recorded on a

Shimadzu FTIR-8400S spectrophotometer and reported in terms of frequency of absorption (cm^{-1}). Only selected IR bands are reported. Chromatographic separations were carried out using Silica Gel 60N (Kanto Chemical Co., Inc.) under the solvent system stated. Thin-layer chromatography (TLC) was performed using Merck Pre-coated TLC plates (silica gel 60 F254). Compound **1b**, **1e**, **1f**, **2a, 2e, 3c, 3n** and each reagents were purchased from Sigma-Aldrich Japan, Wako Pure Chemical Industries and Tokyo Chemical Industry Co., Ltd. Known compounds were prepared according to the published procedures (**1a**[20], **1c**, **1g**, **1h**, **1k**[18], **1d**[21], **2b**, **2c**[22], **2d**[23], **3a**, **3b**, **3d**, **3g**, **3h**[24], **3e**[25], **3f**[26], **3i**[27], **3j**[28], **3l**[29], **3m**[30]). Preparations of **1i**, **1j**, **3k** were described in Supporting information.

General procedure for the synthesis of 5-selanyltriazole (**4a-w**)

CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (9.0 mg, 0.05 mmol, 10 mol%), ethynylstibane (**1**) (0.5 mmol), organic azide (**2**) (0.5 mmol, 1 eq.) and diselenide (**3**) (0.25 mmol, 0.5 eq.) dissolved in DMSO (5 mL) and it was stirred at 60 °C. The reaction time was determined by monitoring with TLC. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The phases were separated and aqueous layer was extracted with CH_2Cl_2 (30 mL x 2). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-hexane/AcOEt).

1-Benzyl-4-phenyl-5-(*p*-tolylselanyl)-1*H*-1,2,3-triazole (**4a**)

176 mg (87%), Colorless plate. Mp 109.5-110 °C (CH_2Cl_2 / hexane); R_f = 0.3 (hexane-AcOEt, 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.8 Hz, 2H, Ar-H), 7.41-7.32 (m, 3H, Ar-H), 7.24-7.22 (m, 5H, Ar-H), 6.93-6.88 (m, 4H, Ar-H), 5.64 (s, 2H, CH_2), 2.23 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3 (s), 137.4 (s), 134.9 (s), 130.6 (s), 130.4 (d), 129.7 (d), 128.6 (d), 128.44 (d), 128.40 (d), 128.0 (d), 127.8 (d), 127.5 (d), 125.7 (s), 118.3 (s), 53.0 (t), 20.9 (q). FTIR (KBr): 1559, 1541, 1508, 1474, 1456 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{19}N_3Se$: 405.0744. Found: 405.0742.

1-Benzyl-5-[(4-methoxyphenyl)selanyl]-4-phenyl-1*H*-1,2,3-triazole (**4b**)

162 mg (77%), Colorless needle. Mp 67-68 °C (Et_2O); R_f = 0.3 (hexane-AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, J = 7.6, 2.0 Hz, 2H, Ar-H), 7.44-7.36 (m, 3H, Ar-H), 7.26-7.19 (m, 5H, Ar-H), 6.96 (d, J = 8.6 Hz, 2H, Ar-H), 6.63 (d, J = 8.9 Hz, 2H, Ar-H), 5.66 (s, 2H, CH_2), 3.71 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4 (s), 151.0 (s), 135.0 (s), 132.2 (d), 130.7 (s), 128.7 (d), 128.43 (d), 128.40 (d), 128.1 (d), 127.7 (d), 127.6 (d), 119.14 (s), 119.09 (s), 115.3 (d), 55.3 (q), 53.0 (t). FTIR (KBr): 1653, 1559, 1489, 1456, 1248 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{19}N_3OSe$: 421.0693. Found: 421.0701.

1-Benzyl-4-phenyl-5-(phenylselanyl)-1*H*-1,2,3-triazole[14] (**4c**)

146 mg (75%), Colorless needle. Mp 91.5-92 °C (CH_2Cl_2 / hexane); R_f = 0.3 (hexane-AcOEt, 5 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.3 Hz, 2H, Ar-H), 7.42-7.33 (m, 3H, Ar-H), 7.25-7.20 (m, 5H, Ar-H), 7.17-7.09 (m, 3H, Ar-H), 6.97 (dd, J = 7.9, 0.7 Hz, 2H, Ar-H), 5.66 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (s), 134.5 (s), 130.5 (s), 129.7 (d), 129.6 (s), 128.6 (d), 129.2 (d), 128.5 (d), 128.4 (d), 128.2 (d), 127.9 (d), 127.4 (d), 127.2 (d), 117.8 (s), 53.1 (t). HRMS: *m/z* $[M]^+$ calcd for $C_{21}H_{17}N_3Se$: 391.0588. Found: 391.0590.

1-Benzyl-5-[(4-chlorophenyl)selanyl]-4-phenyl-1*H*-1,2,3-triazole (**4d**)

151 mg (71%), Colorless plate. Mp 142-144 °C (CH_2Cl_2 / hexane); R_f = 0.5 (hexane-AcOEt, 5 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, J = 7.9, 1.0 Hz, 2H, Ar-H), 7.25-7.15 (m, 5H, Ar-H), 7.45-7.33 (m, 3H, Ar-H), 7.02 (d, J = 6.6 Hz, 2H, Ar-H), 6.82 (d, J = 6.6 Hz, 2H, Ar-H), 5.67 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7 (s), 134.6 (s), 133.5 (s), 130.5 (d), 130.3 (s), 129.7 (d), 128.7 (d), 128.5 (d), 128.2 (d), 127.8 (d), 127.6 (s), 127.4 (d), 117.4 (s), 53.3 (t). FTIR (KBr): 3084, 1559, 1474, 1456, 1227 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{21}H_{16}ClN_3Se$: 425.0198. Found: 425.0201.

Ethyl 4-[(1-benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)selanyl]benzoate (**4e**)

190 mg (82%), Colorless prism. Mp 112.5-113 °C (CH_2Cl_2 / hexane); R_f = 0.3 (hexane-AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 7.8, 1.5 Hz, 2H, Ar-H), 7.73 (d, J = 8.3 Hz, 2H, Ar-

H), 7.41-7.32 (m, 3H, Ar-H), 7.23-7.18 (m, 5H, Ar-H), 6.93 (d, *J* = 8.3 Hz, 2H, Ar-H), 5.67 (s, 2H, CH_2), 4.33 (q, *J* = 7.0 Hz, 2H, CH_2), 1.36 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 (s), 152.0 (s), 136.1 (s), 134.5 (s), 130.5 (d), 130.2 (s), 129.1 (s), 128.74 (d), 128.68 (d), 128.5 (d), 128.3 (d), 128.0 (d), 127.9 (d), 127.3 (d), 116.5 (s), 61.1 (t), 53.3 (t), 14.3 (q). FTIR (KBr): 3028, 1715, 1589, 1396, 1271 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{24}H_{21}N_3O_2Se$: 463.0799. Found: 463.0803.

1-Benzyl-4-phenyl-5-{[4-(trifluoromethyl)phenyl]selanyl}-1*H*-1,2,3-triazole (**4f**)

224 mg (98%), Colorless needle. Mp 103-104 °C (CH_2Cl_2 / hexane); R_f = 0.5 (hexane-AcOEt, 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 6.6, 1.6 Hz, 2H, Ar-H), 7.42-7.34 (m, 3H, Ar-H), 7.26 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.18-7.10 (m, 5H, Ar-H), 6.93 (d, *J* = 8.2 Hz, 2H, Ar-H), 5.68 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2 (s), 134.7 (s), 134.3 (s), 130.1 (s), 129.0 (s, $^2J_{C,F}$ = 33 Hz), 128.8 (d), 128.62 (d), 128.58 (d), 128.4 (d), 128.3 (d), 127.9 (d), 127.3 (d), 126.2 (d, $^3J_{C,F}$ = 4.1 Hz), 123.7 (s, $^1J_{C,F}$ = 271 Hz), 116.3 (s), 53.4 (t). FTIR (KBr): 2922, 1474, 1456, 1398, 1325 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{16}F_3N_3Se$: 459.0462. Found: 459.0459.

1-Benzyl-5-(1-naphthylselanyl)-4-phenyl-1*H*-1,2,3-triazole (**4g**)

185 mg (84%), Colorless prism. Mp 88-90 °C (CH_2Cl_2 / hexane); R_f = 0.3 (hexane-AcOEt, 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 7.8, 1.5 Hz, 2H, Ar-H), 8.01-7.99 (m, 1H, Ar-H), 7.84-7.82 (m, 1H, Ar-H), 7.65 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.55-7.52 (m, 2H, Ar-H), 7.39-7.31 (m, 3H, Ar-H), 7.17-7.11 (m, 5H, Ar-H), 7.06 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.80 (d, *J* = 6.8 Hz, 1H, Ar-H), 5.61 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0 (s), 134.6 (s), 134.1 (s), 132.0 (s), 130.4 (s), 128.8 (d), 128.6 (d), 128.5 (d) x 2, 128.3 (s), 128.1 (d), 127.9 (d), 127.8 (d), 127.6 (d), 127.5 (d), 126.9 (d), 126.5 (d), 126.2 (d), 125.1 (d), 117.3 (s), 53.2 (t). FTIR (KBr): 3026, 1559, 1506, 1472, 1456 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{19}N_3Se$: 441.0744. Found: 441.0747.

1-Benzyl-4-phenyl-5-(*o*-tolylselanyl)-1*H*-1,2,3-triazole (**4h**)

164 mg (81%), Colorless plate. Mp 82-83 °C (Et_2O); R_f = 0.4 (hexane-AcOEt, 4 : 1). ^{1}H NMR (400

MHz, $CDCl_3$): δ = 8.00 (dd, *J* = 8.3, 2.0 Hz, 2H, Ar-H), 7.41-7.33 (m, 3H, Ar-H), 7.22 (s, 5H, Ar-H), 7.13 (d, 1H, *J* = 7.3 Hz, Ar-H), 7.06 (t, 1H, *J* = 7.6 Hz, Ar-H), 6.82 (t, 1H, *J* = 7.6 Hz, Ar-H), 6.47 (d, *J* = 7.8 Hz, 1H, Ar-H), 5.62 (s, 2H, CH_2), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0 (s), 136.4 (s), 134.7 (s), 130.6 (d), 130.5 (s), 128.6 (d), 128.5 (d), 128.4 (d), 128.17 (d), 128.16 (d), 127.9 (d), 127.4 (d), 127.3 (d), 126.9 (d), 117.2 (s), 53.1 (t), 21.9 (q). FTIR (KBr): 3053, 1497, 1464, 1451, 1425 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{19}N_3Se$: 405.0744. Found: 405.0740.

1-Benzyl-5-(mesitylselanyl)-4-phenyl-1*H*-1,2,3-triazole (**4i**)

159 mg (73%), Colorless prism. Mp 107-108.5 °C (CH_2Cl_2 / hexane); R_f = 0.4 (hexane-AcOEt, 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 6.6, 1.5 Hz, 2H, Ar-H), 7.41-7.32 (m, 3H, Ar-H), 7.26-7.23 (m, 3H, Ar-H), 7.01-6.99 (m, 2H, Ar-H), 6.73 (s, 2H, Ar-H), 5.42 (s, 2H, CH_2), 2.18 (s, 3H, CH_3), 2.13 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8 (s), 141.4 (s), 139.0 (s), 134.9 (s), 130.7 (s), 129.4 (d), 128.6 (d), 128.2 (d), 128.2 (d), 127.9 (d), 127.8 (d), 126.9 (d), 125.6 (s), 120.1 (s), 52.7 (t), 23.6 (q), 20.8 (q). FTIR (KBr): 2918, 1456, 1422, 1398, 1234 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{24}H_{23}N_3Se$: 433.1057. Found: 433.1055.

1-{2-[(1-Benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)selanyl]phenyl}-*N*,*N*-dimethylmethanamine (**4j**)

156 mg (70%), Yellow oil. R_f = 0.3 (hexane-AcOEt, 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 8.8, 1.5 Hz, 2H, Ar-H), 7.39-7.29 (m, 3H, Ar-H), 7.19-7.15 (m, 5H, Ar-H), 7.11 (d, *J* = 6.3 Hz, 1H, Ar-H), 7.02 (td, *J* = 7.3, 1.0 Hz, 1H, Ar-H), 6.81 (td, *J* = 7.3, 1.5 Hz, 1H, Ar-H), 6.52 (d, *J* = 7.8 Hz, 1H, Ar-H), 5.57 (s, 2H, CH_2), 3.49 (s, 2H, CH_2), 2.23 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5 (s), 138.5 (s), 135.1 (s), 133.2 (s), 131.2 (s), 129.4 (d), 129.2 (d), 128.4 (d), 128.3 (d), 128.1 (d), 127.91 (d), 127.88 (d), 127.2 (d), 126.0 (d), 121.9 (s), 64.3 (t), 53.0 (t), 43.9 (q). FTIR (neat): 2781, 1464, 1456, 1435, 1364 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{24}H_{24}N_4Se$: 448.1166. Found: 448.1170.

2-[(1-Benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)selanyl]-*N*-(*p*-tolyl)benzamide (**4k**)

169 mg (65%), Colorless needle. Mp 222-222.5 °C (CH_2Cl_2 / hexane); R_f = 0.5 (hexane-AcOEt, 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (dd, *J* = 8.3, 1.5 Hz, 2H, Ar-H), 7.91 (s, 1H, NH), 7.64 (dd, *J* = 7.8, 1.0 Hz, 1H, Ar-H), 7.54 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.36-7.26 (m, 3H, Ar-H), 7.24-7.09 (m, 8H, Ar-H), 6.96 (td, *J* = 8.3, 1.2 Hz, 1H, Ar-H), 6.43 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar-H), 5.65 (s, 2H, CH_2), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7 (s), 152.1 (s), 135.0 (s), 134.71 (s), 134.67 (s), 132.2 (d), 131.5 (s), 130.7 (s), 129.7 (d), 129.1 (d), 128.5 (d), 128.4 (d), 128.2 (d), 128.0 (d), 127.2 (d), 126.9 (d), 125.9 (d), 120.7 (d), 120.0 (s), 53.1 (t), 20.9 (q). FTIR (KBr): 3335, 1645, 1595, 1529, 1323 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{29}H_{24}N_4OSe$: 524.1115. Found: 524.1112.

1-Benzyl-4-phenyl-5-(thiophen-2-ylselanyl)-1*H*-1,2,3-triazole (**4l**)

133 mg (67%), Colorless needle. Mp 120.5-122 °C (CH_2Cl_2 / hexane); R_f = 0.4 (hexane-AcOEt, 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 7.8, 1.5 Hz, 2H, Ar-H), 7.44 (t, *J* = 7.3 Hz, 2H, Ar-H), 7.40-7.23 (m, 7H, Ar-H), 6.87 (d, *J* = 3.9 Hz, 1H, Ar-H), 6.79 (t, *J* = 5.4 Hz, 1H, Ar-H), 5.75 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7 (s), 135.1 (s), 134.6 (d), 131.1 (d), 130.6 (s), 128.8 (d), 128.6 (d), 128.4 (d), 128.2 (d), 127.9 (d), 127.8 (d), 127.6 (d), 121.8 (s), 119.7 (s), 53.1 (t). FTIR (KBr): 3028, 1472, 1454, 1337, 1219 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{19}H_{15}N_3SSe$: 397.0152. Found: 397.0151.

5-(Benzo[*b*]thiophen-2-ylselanyl)-1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**4m**)

122 mg (60%), Colorless needle. Mp 137-139 °C (CH_2Cl_2 / hexane); R_f = 0.5 (hexane-AcOEt, 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (dd, *J* = 8.3, 1.5 Hz, 2H, Ar-H), 7.62 (dd, *J* = 7.3, 1.0 Hz, 1H, Ar-H), 7.53 (dd, *J* = 6.8, 2.9 Hz, 1H, Ar-H), 7.47-7.37 (m, 3H, Ar-H), 7.30-7.19 (m, 7H, Ar-H), 7.01 (s, 1H, Ar-H), 5.75 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3 (s), 142.4 (s), 139.5 (s), 135.0 (s), 130.4 (s), 129.4 (d), 128.70 (s), 128.68 (d), 128.5 (d), 128.2 (d), 127.8 (d), 127.6 (d), 125.4 (s), 124.8 (d), 124.6 (d), 123.2 (d), 121.7 (d), 118.2 (s), 53.3 (t). FTIR (KBr): 1495, 1454, 1427, 1343, 1223 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{17}N_3SSe$: 447.0308. Found: 447.0308.

1-Benzyl-5-(benzylselanyl)-4-phenyl-1*H*-1,2,3-triazole (**4n**)

77 mg (38%), Colorless needle. Mp 90-91.5 °C (CH_2Cl_2 / hexane); R_f = 0.4 (hexane-AcOEt, 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 8.3, 1.5 Hz, 2H, Ar-H), 7.45-7.10 (m, 11H, Ar-H), 6.83 (dd, J = 6.6, 2.9 Hz, 2H, Ar-H), 5.32 (s, 2H, CH_2), 3.59 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8 (s), 136.9 (s), 135.5 (s), 130.8 (s), 128.8 (d), 128.62 (d), 128.57 (d), 128.4 (d), 128.3 (d), 128.2 (d), 127.8 (d), 127.5 (d), 127.2 (d), 118.1 (s), 52.5 (t), 33.3 (t). FTIR (KBr): 1495, 1458, 1429, 1340, 1217 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{19}N_3Se$: 405.0744. Found: 405.0747.

1-Benzyl-4-(4-methoxyphenyl)-5-(phenylselanyl)-1*H*-1,2,3-triazole (**4o**)

158 mg (75%), Colorless plate. Mp 96-97 °C (Et_2O); R_f = 0.3 (hexane-AcOEt, 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.22-7.16 (m, 5H, Ar-H), 7.16-7.08 (m, 3H, Ar-H), 6.98-6.90 (m, 4H, Ar-H), 5.64 (s, 2H, CH_2), 3.82 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (s), 151.5 (s), 134.9 (s), 129.73 (s), 129.67 (d), 129.1 (d), 128.8 (d), 128.6 (d), 128.2 (d), 127.9 (d), 127.1 (d), 123.0 (s), 116.9 (s), 113.9 (d), 55.2 (q), 53.1 (t). FTIR (KBr): 1539, 1478, 1456, 1260, 1245 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{19}N_3OSe$: 421.0693. Found: 421.0690.

1-Benzyl-5-(phenylselanyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (**4p**)

135 mg (73%), Colorless plate. Mp 79-81 °C (Et_2O); R_f = 0.3 (hexane-AcOEt, 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.24-7.16 (m, 7H, Ar-H), 7.16-7.08 (m, 3H, Ar-H), 6.96 (dd, *J* = 7.8, 1.5 Hz, 2H, Ar-H), 5.64 (s, 2H, CH_2), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7 (s), 138.5 (s), 134.8 (s), 129.7 (s), 129.6 (d), 129.2 (d), 129.1 (d), 128.6 (d), 128.1 (d), 127.9 (d), 127.6 (s), 127.3 (d), 127.1 (d), 117.3 (s), 53.1 (t), 21.3 (q). FTIR (KBr): 1576, 1478, 1456, 1439, 1335 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{19}N_3Se$: 405.0744. Found: 405.0742.

1-Benzyl-5-(phenylselanyl)-4-[4-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole (**4q**)

167 mg (73%), Colorless needle. Mp 112-114 °C (CH_2Cl_2 / hexane); R_f = 0.3 (hexane-AcOEt, 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.64 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.26-

7.09 (m, 8H, Ar-H), 6.96 (dd, *J* = 7.8, 1.0 Hz, 2H, Ar-H), 5.68 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0 (s), 134.6 (s), 134.0 (s), 130.0 (s, $^2J_{C,F}$ = 32 Hz), 129.8 (d), 129.3 (d), 129.1 (s), 128.7 (d), 128.3 (d), 127.6 (d), 127.55 (d), 127.53 (d), 125.4 (d, $^3J_{C,F}$ = 3.3 Hz), 124.1 (s, $^1J_{C,F}$ = 271 Hz), 118.8 (s), 53.3 (t). FTIR (KBr): 1559, 1497, 1456, 1417, 1234 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{22}H_{16}F_3N_3Se$: 459.0462. Found: 459.0465.

1-Benzyl-4-(cyclohex-1-en-1-yl)-5-(phenylselanyl)-1*H*-1,2,3-triazole (**4r**)

145 mg (74%), Yellow oil. R_f = 0.3 (hexane-AcOEt, 5 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.11 (m, 8H, Ar-H), 6.96 (dd, *J* = 8.3, 2.0 Hz, 2H, Ar-H), 6.47-6.45 (m, 1H, cyclohexene), 5.58 (s, 2H, CH_2), 2.58-2.54 (m, 2H, cyclohexene), 2.17-2.11 (m, 2H, cyclohexene), 1.73-1.69 (m, 2H, cyclohexene), 1.63-1.58 (m, 2H, cyclohexene). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4 (s), 135.0 (s), 130.1 (s), 129.5 (d), 129.2 (d), 129.0 (d), 128.6 (d), 128.1 (s), 128.0 (d), 127.8 (d), 127.0 (d), 116.6 (s), 52.9 (t), 27.0 (t), 25.6 (t), 22.6 (t), 21.9 (t). FTIR (neat): 1576, 1497, 1478, 1437, 1323 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{21}H_{21}N_3Se$: 395.0901. Found: 395.0902.

1-Benzyl-4-butyl-5-(phenylselanyl)-1*H*-1,2,3-triazole[13] (**4s**)

154 mg (83%), Yellow oil. R_f = 0.4 (hexane-AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.10 (m, 8H, Ar-H), 6.96 (dd, *J* = 8.3, 1.0 Hz, 2H, Ar-H), 5.57 (s, 2H, CH_2), 2.72 (t, *J* = 7.8 Hz, 2H, CH_2), 1.63 (quit, *J* = 7.7 Hz, 2H, CH_2), 1.32 (sext, *J* = 7.4 Hz, 2H, CH_2), 0.87 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2 (s), 135.0 (s), 129.7 (d), 129.6 (s), 129.5 (d), 128.6 (d), 128.1 (d), 127.9 (d), 127.2 (d), 119.1 (s), 53.1 (t), 31.4 (t), 25.6 (t), 22.4 (t), 13.7 (q). HRMS: *m/z* $[M]^+$ calcd for $C_{19}H_{21}N_3Se$: 371.0901. Found: 371.0905.

1-Cinnamyl-4-phenyl-5-(phenylselanyl)-1H-1,2,3-triazole (**4t**)

119 mg (57%), Colorless oil. R_f = 0.3 (hexane-AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 6.8 Hz, 2H, Ar-H), 7.44-7.34 (m, 4H, Ar-H), 7.24-7.12 (m, 9H, Ar-H), 6.49 (d, *J* = 15.6 Hz, 1H, -CH=CH-), 6.22-6.14 (m, 1H, -CH=CH-), 5.24 (d, *J* = 6.3 Hz, 2H, CH_2). ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 135.7 (s), 134.8 (d), 130.6 (s), 129.83 (d), 129.76 (s), 129.5 (d), 128.6 (d), 128.49 (d), 128.46 (d), 128.2 (d), 127.5 (d), 127.4 (d), 126.6 (d), 122.2 (d), 51.6 (t). FTIR (neat): 3057, 1576, 1476, 1449, 1439 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{23}H_{19}N_3Se$: 417.0744. Found: 417.0747.

Ethyl 2-{4-phenyl-5-(phenylselanyl)-1*H*-1,2,3-triazol-1-yl}acetate (**4u**)

100 mg (52%), Colorless plate. Mp 80.5-81.5 °C (AcOEt / hexane); R_f = 0.3 (hexane- AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.07 (m, 2H, Ar-H), 7.44-7.34 (m, 3H, Ar-H), 7.22-7.14 (m, 5H, Ar-H), 5.24 (s, 2H, CH_2), 4.12 (q, 2H, *J* = 7.2 Hz, CH_2), 1.21 (t, 3H, *J* = 7.1 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1 (s), 151.1 (s), 130.3 (s), 129.8 (d), 128.9 (s), 128.6 (d), 128.5 (d), 127.6 (d), 127.4 (d), 118.9 (s), 62.3 (t), 50.3 (t), 14.0 (q). FTIR (KBr): 3024, 1750, 1554, 1478, 1248 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{18}H_{17}N_3O_2Se$: 387.0486. Found: 387.0488.

1-(Naphthalen-1-ylmethyl)-4-phenyl-5-(phenylselanyl)-1*H*-1,2,3-triazole (**4v**)

137 mg (62%), Colorless plate. Mp 126.5-128.0 °C (AcOEt / hexane); R_f = 0.4 (hexane- AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, 1H, *J* = 7.8 Hz, Ar-H), 8.08 (d, 2H, *J* = 7.3 Hz, Ar-H), 7.83 (dd, 1H, *J* = 7.8, 2.0 Hz, Ar-H), 7.72 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.56-7.47 (m, 2H, Ar-H), 7.42-7.32 (m, 3H, Ar-H), 7.23 (t, 1H, *J* = 8.3 Hz, Ar-H), 7.12-7.00 (m, 4H, Ar-H), 6.93 (d, 2H, *J* = 8.3 Hz, Ar-H), 6.12 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5 (s), 133.6 (s), 130.7 (s), 130.5 (s), 130.4 (s), 129.5 (d), 129.4 (s), 129.3 (d), 128.9 (d), 128.8 (d), 128.6 (d), 128.5 (d), 127.5 (d), 127.2 (d), 126.7 (d), 126.4 (d), 126.0 (d), 125.1 (d), 122.9 (d), 118.3 (s), 51.0 (t). FTIR (KBr): 3055, 1576, 1476, 1441, 1339 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{19}N_3Se$: 441.0744. Found: 441.0741.

4-Phenyl-5-(phenylselanyl)-1-{(phenylthio)methyl}-1*H*-1,2,3-triazole (**4w**)

125 mg (59%), Yellow oil. R_f = 0.4 (hexane-AcOEt, 4 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.41-7.25 (m, 8H, Ar-H), 7.20-7.08 (m, 5H, Ar-H), 5.71 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2 (s), 132.9 (d), 132.1 (s), 130.2 (s), 129.7 (d), 129.5 (d), 129.4 (s), 129.2 (d), 128.6 (d), 128.4 (d), 127.5 (d), 127.3 (d), 117.8 (s), 53.5 (t). FTIR (neat): 1559, 1506, 1474,

1439, 1341 cm^{-1}. HRMS: *m/z* $[M]^+$ calcd for $C_{21}H_{17}N_3SSe$: 423.0308. Found: 423.0310.

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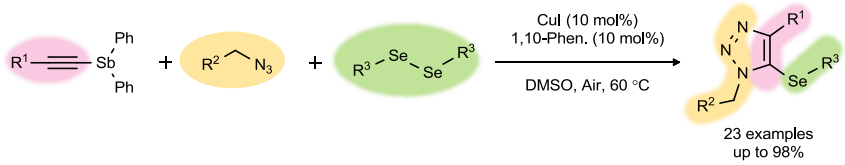
Graphical abstract



Short text

Cu-catalyzed three-component reaction of ethynylstibanes, organic azides, and diaryl diselenides under aerobic conditions led to the formation of fully substituted 5-selanyl-1,2,3-triazoles in moderate to excellent yields. Ethynylstibanes having antimony atom gave superior results compared to various alkynes having other typical elements such as silicon, tin, and tellurium.

Key Topic

Three-component reaction

Reaction of organoantimony