Silver-catalyzed carbon-selenium cross coupling using *N*-(phenylseleno)phthalimide: an alternate approach to the synthesis of organoselenides

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ABSTRACT

Silver(I) catalyzed phenylselenylation of terminal alkynes and organoboronic acids has been demonstrated using *N*-(phenylseleno)phthalimide as electrophilic SePh donor. A wide variety of terminal alkynes and organoboronic acids are selenylated efficiently to produce the corresponding alkynyl and diaryl selenides respectively in good yields. Silver(I) acts as a Lewis acid in this process.

Keywords: silver catalysis, selenylation, *N*-(phenylseleno)phthalimide, alkynyl selenide, diaryl selenide.

Graphical abstract

Silver-catalyzed carbon-selenium cross coupling using *N*-(phenylseleno)phthalimide: an alternate approach to the synthesis of organoselenides

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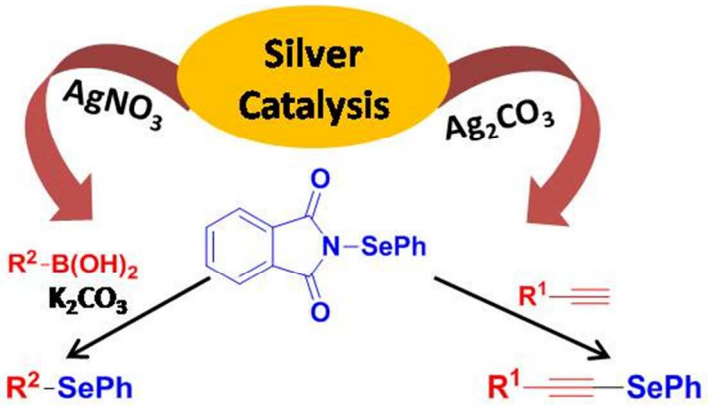

Introduction

Organoselenium compounds are of immense importance due to their occurrence in many micronutrients,[1] biologically active molecules[2] and natural products.[3] They have potential applications in the field of pharmaceutical chemistry,[4] organic synthesis[5] and material science.[6] One of the efficient tools for the synthesis of organoselenium compounds is cross coupling with suitable selenylating reagents in the presence of a transition metal (Cu,[7] Pd,[8] Ni,[9] Ru,[10] Rh[11]) catalyst. The commonly used selenylating reagents include PhSeSePh,[7a-e,8a,10-12] PhSeCl,[11,13] PhSeBr,[7f,14] PhSeCN.[7g,15] However, these selenylating reagents are associated with one or more drawbacks, such as lower stability, generation of toxic vapour and reactive byproducts.[16] A better alternative selenium source is the less explored *N*-(phenylseleno)phthalimide (NPSP)[17] which exists as odourless and colourless stable crystalline solid.

Thus we are interested to investigate selenylation using *N*-(phenylseleno)phthalimide (NPSP) as the benign source of SePh in presence of a suitable metal catalyst. Palladium, copper and nickel catalysts being considerably active have been widely used for cross coupling reactions.[18] On the other hand, among the noble metals silver catalyst is moderately active and has been used for coupling reaction in a limited way.[19] Earlier, NPSP was involved in the enantioselective selenylation of aldehydes using different organocatalysts such as L-proline,[20] TMS-protected α,α-diphenyl-2-pyrrolidinemethanol,[21] and diphenylprolinol silyl ether,[22] enantioselective selenoloactonization using $(DHQD)_2PHAL$

(1,4-bis[(S)-[(2R,4S,5R)-5-ethylquinuclidin-2-yl]-(6-ethoxy-4-quinolyl)methoxy]phthalazine)[23a] and selenylation of olefins under the catalysis of p-TsOH.[23b] As NPSP releases an electrophilic SePh species we consider it appropriate to involve a nucleophilic coupling partner such as

terminal alkyne and organoboronic acid under the catalysis of moderately active metal for an effective selenylation. With this concept we report here a simple and general method for phenylsenylation of alkynes/organoboronic acids using NPSP and silver catalyst in THF (Scheme 1).

Scheme 1.

Reports of C-Se cross-coupling reaction usually invoke the formation of the C-Se bond by reductive elimination from an intermediate transition metal complex **A** of Cu/Pd/Ru/Rh (Scheme 2).[7,8,10,11] It is anticipated that in the present reaction Ag(I) catalyst having moderate Lewis acid activity[19d] is likely to increase the electrophilicity of SePh moiety which will then readily interact with the nucleophilic aryl/alkynyl counterpart.

Scheme 2.

Results and Discussion

To optimize the reaction conditions a series of experiments were conducted with 4-methoxyphenylacetylene as a model substrate for selenylation using NPSP in the presence of Ag(I) catalyst with variation of reaction parameters such as catalyst, solvent, reaction temperature and time (Table 1). The selenylation was not observed using 10 mol% of Ag_2CO_3 in THF at room temperature (25 ^oC) (Table 1, entry 1). However the increase of reaction temperature to 66 ^oC in THF at reflux for12 h made a remarkable improvement (Table 1, entry 2).

Table 1.

Lowering of catalyst loading to 5 mol% and reducing the reaction time to 10 h decreased the yield (Table 1, entries 3 and 4). Use of other solvents, *N*-methylpyrrolidinone (NMP) and toluene at similar conditions did not give better results (Table 1, entries 5 and 6). The involvement of other silver salts such as $AgNO_3$ and $AgOTf/K_2CO_3$ provided comparable yields (Table 1, entries 7 and 8). For comparison, when Cu-salts are used as catalysts in place of Ag marginal yields (20-26 %) of products are obtained in addition to considerable amount of dimerized product of alkyne (Table 1, entries 9 and 10), whereas when other transition metal salts ($Ni(acac)_2$, $Ru(PPh_3)_3Cl_2$, $Co(acac)_2$ and iron nanoparticles) were used no reaction was observed in similar conditions (Table 1, entries, 11, 12, 13 and 14). The reaction did not occur at all in the absence of Ag_2CO_3 (Table 1, entry 15). Thus, in a representative experimental procedure, a mixture of 4-methoxy phenylacetylene (0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol) and Ag_2CO_3 (10 mol%) in dry THF (5 ml) was heated at reflux under argon atmosphere for 12 h. The progress of the reaction was monitored by TLC. Standard work-up followed by purification through column chromatography provided the pure product.

To investigate the substrate scope several diversely substituted terminal alkynes were subjected to selenylation by this procedure. The results are summarized in Table 2 (Chart 1). Both aromatic and aliphatic alkynes were selenylated efficiently with NPSP under the silver catalyzed protocol. Electron donating group, OMe (Table 2, entries 1, 2, 5) as well as electron withdrawing groups, F, CF_3 (Table 2, entries 3, 4) in the aromatic ring did not have much influence in the control of yields. The heteroaryl alkyne, 3-ethynylthiophene was selenylated cleanly by this procedure (Table 2, entry 6). Aliphatic alkynes such as cyclohexyl acetylene (Table 2, entry 7) and ethyl acetylene carboxylate (Table 2, entry 8) participated in the selenylation reaction to give good yields of desired alkynyl selenides.

Table 2.

Being encouraged by the successful selenylation of alkynes using NPSP by this protocol we next employed organoboronic acids as selenylating counterpart. Interestingly, it was observed that use of Ag_2CO_3 under the same experimental conditions (Table 1) was not effective for boronic acids (Table 3, entry 1). However, use of 1 equiv. of K_2CO_3 along with 10 mol % of Ag_2CO_3 improved the yield of the reaction considerably providing 56% yield of **5aa** (Table 3, entry 2)**.** The increase of catalyst loading did not improve the yield of the reaction substantially (Table 3, entry 3). Interestingly, the use of $AgNO_3$ (10 mol%) in place of Ag_2CO_3 together with 1 equiv. of K_2CO_3 in refluxing THF for 12 h produced the diaryl selenide product **5aa** in 82% yield (Table 3, entry 4). However, the best yield was obtained using 20 mol % of $AgNO_3$ (Table 3, entry 5).

Table 3.

Thus several organoboronic acids with wide structural variations were subjected to phenylselenylation with NPSP by the optimized protocol (Table 4, Chart 1). The aryl boronic acids containing electron donating groups (O^iPr, Me) participated in the selenylation reaction to offer the corresponding diaryl selenides in high yields (Table 4, entries 1, 3). The electron-withdrawing groups (OCF_3, NO_2) in the aryl ring did not affect the yield ofproducts (Table 4, entries 2, 8). Phenylselenylation was successfully accomplished with bridged substrate like acenaphthene-5-boronic acid (Table 4, entry 4). The reactions proceeded satisfactorily with substituted styrenyl boronic acids (Table 4, entries 5, 6) and pentynyl boronic acid (Table 4, entry 7) without any difficulty. Naphthyl boronic acid also underwent C-Se cross-coupling by this procedure effectively (Table 4, entry 9).

Table 4.

The reaction of alkyl boronic acid such as Me-$B(OH)_2$ with NPSP under the reaction conditions was also investigated; however the reaction failed to provide the corresponding addition product. To compare the reactivity of NPSP with other $PhSe^+$ sources such as PhSeCN and PhSeBr under the identical reaction conditions we found that the reaction of alkyne with PhSeBr produced the alkynyl selenide, **3aa** only in 48% yield, whereas with PhSeCN only trace (2%) amount of the product was obtained.

Regarding the reaction pathway of this selenylation process we suggest that NPSP initially coordinates with Ag^+, which makes the SePh moiety of NPSP more electrophilic[16,23] (Scheme 3). It is proposed that silver(I) subsequently activates the terminal alkyne[24] to generate silver acetylide type intermediate which interacts with activated NPSP producing the alkynyl selenide product and phthalimide. Ag^+ ion is released in the process and it participates in the next catalytic cycle. In case of organoboronic acid, a base (K_2CO_3) is required to complete the octet of boron atom in boronic acid so that aryl moiety is able to migrate with its bond pair of electrons[25] and it reacts with electrophilic SePh leading to the formation of the diaryl selenide product.

Scheme 3.

$AgNO_3$, having higher effective Lewis acidic activity compared to Ag_2CO_3, works more efficiently in case of C-Se cross-coupling with organoboronic acids.[19e] However, in case of alkyne, the formation of silver-acetylide type intermediate through the interaction of Ag^+ ion and terminal alkyne is realized with comparable efficacy with both the salts, $AgNO_3$ and Ag_2CO_3. Marginally higher activity of Ag_2CO_3 may be attributed to the higher basicity of CO_3^{2-} in comparison to NO_3^-.

Conclusion

In summary, we have developed a convenient and comprehensive method for Ag(I)-catalyzed C-Se bond formation using *N*-(phenylseleno)phthalimide as the mild SePh donor. The phenylselenylation is accomplished efficiently with a broad spectrum of structurally diverse alkynes as well as organoboronic acids. High yields of the products, clean reactions, easy operating procedures and tolerance to various functional groups with structural diversity of the substrates render the protocol synthetically useful. To the best of our knowledge this is the first report of silver catalyzed phenylselenylation using NPSP as the selenium source.

Experimental

General

NMR spectra were recorded at 300, 400 and 500 MHz for ^{1}H and 75, 100 and 125 MHz for ^{13}C spectra in $CDCl_3$ solutions. Elemental analyses were done at our Institute with an autoanalyzer. Ag_2CO_3, $AgNO_3$, *N*-(phenylseleno)phthalimide, K_2CO_3, all acetylenes, and boronic acids were procured commercially.

Representative experimental procedure for the cross-coupling of 4-ethynylanisole and *N*-(phenylseleno)phthalimide (Table 2, 3aa)

A mixture of 4-ethynylanisole (40 mg, 0.3 mmol), *N*-(phenylseleno)phthalimide (60 mg, 0.3 mmol), Ag_2CO_3 (8.2 mg, 0.03 mmol) in THF (3 mL) was heated at reflux under argon for 12 h (TLC). The reaction mixture was then allowed to cool and was extracted with diethyl ether (3 x 20 mL). The extract was washed with water (10 mL) and brine (10 mL). Then the organic phase was dried over Na_2SO_4 and evaporated to leave the crude product, which was purified by column chromatography over silica gel (hexane/diethyl ether 98:2) to provide the pure ((4-methoxyphenyl)ethynyl)(phenyl)selane as yellow gummy liquid, (82 mg, 95%); IR

(neat): ν = 3306, 3140, 3007, 2925, 2851, 2316, 2150, 1595, 1575, 1511, 1470, 1452, 1398, 1296, 1255, 1161 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.87 (dd, J_1 = 2 Hz, J_2 = 6.5 Hz, 2H), 7.27-7.34 (m, 3H), 7.46 (dd, J_1 = 2 Hz, J_2 = 7 Hz, 2H), 7.58 (dd, J_1 = 1 Hz, J_2 = 8.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 67.3, 114.1, 115.4, 127.1, 129.0, 129.4, 129.6, 133.7, 160.1 ppm; anal. calcd. for $C_{15}H_{12}OSe$; C 62.73, H 4.21; found: C 62.77, H 4.28 %.

This procedure was followed for all the reactions listed in Table 2 and Table 4. Although the representative procedure is based on mmol scale reaction scaling up to 10 mmol also produced similar results. All of the known compounds are identified by their spectroscopic data (^1H NMR and ^{13}C NMR) and the data are consistent with those reported earlier. Similarly all of the unknown compounds are well characterized by their spectroscopic and spectrometric data (IR, ^1H NMR, ^{13}C NMR and elemental analysis). All these data are provided in below.

((2-Methoxyphenyl)ethynyl)(phenyl)selane (Table 2, 3ab): Yellow viscous liquid, 90%, 77.54 mg, IR (neat): □ = 3061, 3019, 2160, 1589, 1472, 1425, 1263, 1213 cm^{-1};^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H), 6.88-6.93 (m, 2H), 7.25-7.33 (m, 4H), 7.60 (d, J = 7.5 Hz, 1H), 7.64 (dd, J = 1.5 Hz, 8.7 Hz, 2H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 72.9, 99.8, 110.8, 112.6, 120.5, 126.9, 128.8, 129.5, 130.0, 130.4, 133.5, 134.3, 160.4 ppm; anal. calcd. for $C_{15}H_{12}OSe$; C 62.73, H 4.21; found: C 62.75, H 4.26 %.

((3-Fluorophenyl)ethynyl)(phenyl)selane[7d] (Table 2, 3ac): Viscous liquid, 92%, 75.94 mg, ^1H NMR (400 MHz, $CDCl_3$): δ 6.93-6.97 (m, 1H), 7.09 (dd, J = 1.5 Hz, J = 9.5 Hz, 1H), 7.16-7.21 (m, 3H), 7.22-7.27 (m, 2H), 7.49-7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.1, 101.6 (d, J_{C-F} = 3 Hz), 115.9 (d, J_{C-F} = 21 Hz), 118.5 (d, J_{C-F} = 23 Hz), 125.1 (d, J_{C-F} = 9 Hz), 127.4, 127.6 (d, J_{C-F} = 3 Hz), 128.6, 129.4, 129.7, 130.0, 130.1, 162.4 (d, J_{C-F} = 245 Hz) ppm.

Phenyl((2-(trifluoromethyl)phenyl)ethynyl)selane (Table 2, 3ad): Colourless gummy liquid, 90%, 87.79 mg; IR (neat): ν = 3129, 2925, 2161, 1615, 1585, 1480, 1429, 1388, 1316, 1265, 1171, 1130 cm^{-1} ;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.30 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 3H), 7.66 (d, *J* = 8 Hz, 1H) ppm ; ^{13}C NMR (400 MHz, $CDCl_3$): δ 76.4, 98.9, 121.5 (d, *J* = 2 Hz), 122.3, 125, 126 (q, *J* = 5 Hz), 127.4, 128, 128.5, 129.5 (q, *J* = 7 Hz), 131, 131.4 (d, *J* = 17 Hz), 133.9 ppm; anal. calcd. for $C_{15}H_9F_3Se$; C 55.40, H 2.79; found: C 55.37, H 2.77 %.

(6-Methoxynaphthalen-2-yl)(phenyl)selane[7d] (Table 2, 3ae): Colourless gummy liquid, 95%, 89.26 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.10-7.18 (m, 2H), 7.27-7.34 (m, 3H), 7.51 (dd, J_1 = 1.5Hz, J_2 = 8.4Hz, 1H), 7.60-7.71 (m, 4H), 7.95(s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 68.7, 103.6, 106.0, 118.2, 119.6, 126.9, 127.2, 128.5, 129.1, 129.2, 129.2, 129.5, 129.7, 131.8, 134.5, 158.6 ppm.

3-((Phenylselanyl)ethynyl)thiophene (Table 2, 3af): Colourless gummy liquid, 75%, 59 mg; IR (neat): ν = 3306, 3119, 2925, 2851, 1636, 1575, 1480, 1399, 1316, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (dd, J_1 = 5.1, J_2 = 0.9 Hz, 1H), 7.26-7.36 (m, 4H), 7.53-7.59 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.9, 97.9, 116.3, 122.4, 125.4, 127.2, 129.0, 129.2, 129.7, 129.9, 130.2ppm; anal. calcd. for $C_{12}H_8SSe$; C 54.76, H 3.06; found: C 54.78, H 3.03 %.

(Cyclohexylethynyl)(phenyl)selane (Table 2, 3ag): Yellow gummy liquid, 92%, 72.6 mg; IR (neat): ν = 3305, 3140, 2935, 2851, 1636, 1575, 1480, 1440, 1399, 1109, 1007cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23-1.26 (m, 3H), 1.42-1.48 (m, 3H), 1.64-1.68 (m, 2H), 1.77-1.80 (m, 2H), 2.53-2.57 (m, 1H), 7.11-7.15 (m, 1H), 7.17-7.22 (m, 2H), 7.41-7.43 (m, 2H) ppm; ^{13}C NMR

(75 MHz, $CDCl_3$): δ24.9, 25.9, 30.4, 31.0, 32.8, 57.5, 109.0, 126.7, 128.5, 128.6, 129.4, 129.7 ppm; anal. calcd. for $C_{14}H_{16}Se$; C 63.88, H 6.13; found: C 63.82, H 6.17 %.

Ethyl 3-(phenylselanyl)propiolate (Table 2, 3ah): Yellow gummy liquid, 90%, 68.35 mg; IR (neat):ν = 3398, 3305,3129, 2976, 2925, 2851, 2150, 1697, 1575, 1480, 1441, 1392, 1368, 1245, 1099, 1017, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, J = 5.6Hz, 3H), 4.25 (q, J = 5.6Hz, 2H), 7.30-7.37 (m, 3H), 7.59 (dd, J_1 = 1.2Hz, J_2 = 6.4Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): 14.2, 62.1, 74.9, 96.4, 116.2, 126.2, 128.3, 130.0, 130.3, 152.80 ppm; anal. calcd. for $C_{11}H_{10}OSe$; C 52.19, H 3.98; found: C 52.23, H 3.94 %.

((4-Phenoxyphenyl)ethynyl)(phenyl)selane (Table 2, 3ai): Yellow gummy liquid, 89%, 93.2 mg; IR (neat): ν = 3295, 3140, 2925, 2851, 2150, 1570, 1490, 1429, 1388, 1245, 1192, 1151, 1109, 1017, 872 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$): δ 6.95 (dd, J_1 = 9, J_2 = 2.5 Hz, 2H), 7.04 (d, J = 8 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.25-7.28 (m, 1H), 7.32-7.39 (m, 4H), 7.46-7.49 (m, 2H), 7.57-7.60 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.4, 102.6, 117.8, 118.4, 119.6, 124.1, 127.2, 129.1, 129.2, 129.6, 130.0, 133.7, 156.4, 158.1 ppm; anal. calcd. for $C_{20}H_{14}OSe$; C 68.77, H 4.04; found: C 68.73, H 4.08 %.

(3-Isopropoxyphenyl)(phenyl)selane (Table 4, 5aa): Yellow gummy liquid, 96%, 83.8 mg; IR (neat): ν = 3140, 2976, 2935, 2851, 1718, 1585, 1480, 1440, 1378, 1276, 1245, 1171, 1120, 1017, 946 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (d, J = 6Hz, 6H), 4.54 (m, 1H), 6.83 (dd, J_1 = 2 Hz, J_2 = 6.5 Hz, 2H), 7.19-7.22 (m, 3H), 7.33-7.35 (m,2H), 7.48 (dd, J = 2Hz, J = 6.5 Hz,2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 22.1, 70.1, 76.85, 117.0, 119.7, 126.5, 129.27, 131.1, 133.39, 136.6, 138.3, 158.3 ppm; anal. calcd. for $C_{15}H_{16}OSe$; C 61.86, H 5.54; found: C 61.44, H 5.14 %.

Phenyl(4-(trifluoromethoxy)phenyl)selane (Table 4, 5ab): Yellow gummy liquid, 85%, 80.9 mg; IR (neat): ν = 3130, 2915, 1636, 1398, 1181, 1110, 987, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (dd, J_1 = 1.2 Hz, J_2 = 9 Hz, 2H), 7.28-7.33 (m, 3H), 7.43-7.51(m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.9, 122.2, 128.0, 129.6, 130.0, 130.4, 133.6, 134.0, 148.6 ppm; anal. calcd. for $C_{13}H_9F_3OSe$; C 49.23, H 2.86; found: C 49.27, H 2.88 %.

Phenyl(*o*-tolyl)selane[26] (Table 4, 5ac): Yellow liquid, 89%, 66 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.10-7.13 (m, 1H), 7.23-7.39 (m,5H), 7.40-7.46 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 22.4, 126.8, 127.2, 127.9, 129.4, 130.3, 130.9, 131.8, 132.8, 133.8, 140.0 ppm.

(1,2-Dihydroacenaphthylen-5-yl)(phenyl)selane (Table 4, 5ad): Colourless gummy liquid, 97%, 90 mg; IR (neat): ν = 3110, 2815, 1436, 1371, 1281, 1141 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ 3.25-3.33 (m, 4H), 7.05-7.08 (m, 3H), 7.13-7.16 (m, 1H), 7.18-7.22 (m, 3H), 7.35-7.44 (m, 1H), 7.76 (dd, J_1 = 5.6 Hz, J_2 = 24 Hz, 2H) ppm; ^{13}CNMR (100 MHz, $CDCl_3$): δ 30.2, 30.6, 120.0, 122.7, 122.9, 126.3, 128.9, 129.2, 130.6, 132.9, 133.5, 136.9, 140.0, 146.5, 148.2 ppm; anal. calcd. for $C_{18}H_{14}Se$; C 69.91, H 4.56; found: C 69.27, H 4.48 %.

(*E*)-(4-Methylstyryl)(phenyl)selane[7b] (Table 4, 5ae): Yellow gummy liquid, 92%, 75.4 mg; ^{1}H NMR (500 MHz, $CDCl_3$)**: δ** 2.33 (s, 3H), 6.89 (dd, J_1 = 4 Hz, J_2 = 15.5 Hz, 1H), 7.10-7.14 (m, 3H), 7.23-7.33 (m, 5H), 7.53-7.55 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 117.9, 126.1, 127.4, 129.4, 129.5, 130.6, 132.4, 134.4, 135.8, 137.7 ppm.

(*E*)-(4-Methoxystyryl)(phenyl)selane[7a] (Table 4, 5af): Yellow gummy liquid, 90%, 78.1 mg; ^{1}H NMR (300 MHz, $CDCl_3$): δ3.81 (s, 3H), 6.85-6.91 (m, 3H), 7.02 (d, J = 15.6 Hz, 1H), 7.25-

7.31 (m, 5H), 7.52-7.55 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 114.2, 116.0, 127.2, 127.5, 129.4, 130.0, 130.9, 132.1, 136.0, 159.5 ppm.

Pent-1-yn-1-yl(phenyl)selane[27] (Table 4, 5ag): Yellow gummy liquid, 93%, 63 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, J = 7.6 Hz, 3H), 1.65 (sextet, J = 7.2 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 7.23-7.34 (m, 3H), 7.53-7.55 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 22.3, 22.7, 57.7, 76.8, 104.6, 126.8, 128.7, 129.5 ppm.

(3-Nitrophenyl)(phenyl)selane[12b] (Table 4, 5ah): Yellow gummy liquid, 80%, 66.7 mg; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.36-7.41(m, 4H), 7.56-7.59 (m, 2H), 7.63-7.66 (m, 1H), 8.03-8.06 (m,1H), 8.20 (t, J = 2.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.7, 125.9, 128.6, 128.9, 129.9, 130.0, 134.9, 137.1, 148.8 ppm.

Naphthalen-2-yl(phenyl)selane[7b] (Table 4, 5ai): Yellow gummy liquid, 74%, 62.9 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (dd, J_1 = 6.3 Hz, J_2 = 3.3 Hz, 3H), 7.44-7.54 (m, 5H), 7.73 (d, J = 7.8 Hz, 2H), 7.78-7.82 (m, 1H), 7.99 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.3, 126.6, 127.5, 127.9, 128.6, 128.9, 129.5, 130.6, 131.3, 132.2, 132.6, 133.0, 134.1 ppm.

Supplementary Material

Supplementary material is available with the article through the journal website at …… Supplementary material includes the ^{1}H NMR and ^{13}C NMR spectra of all synthesized compounds listed in Table 2 and Table 4.

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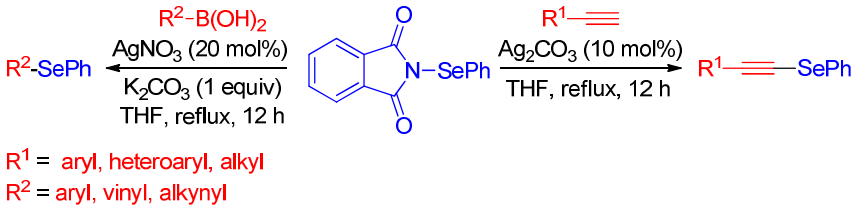
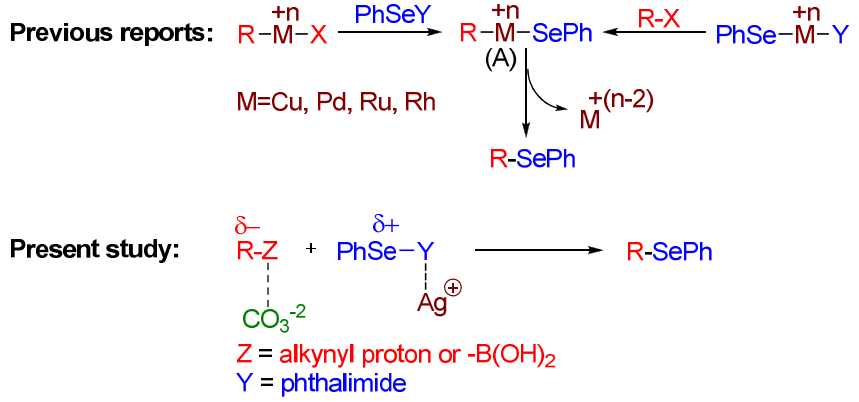
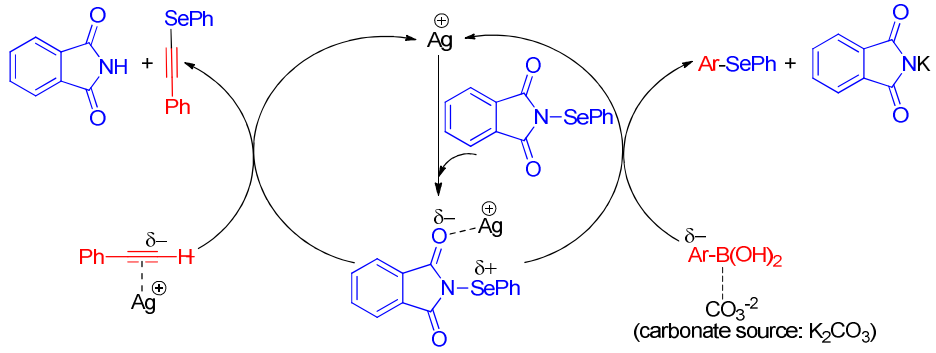


Scheme 1. Silver catalyzed phenylselenylation of alkynes and organoboronic acids.

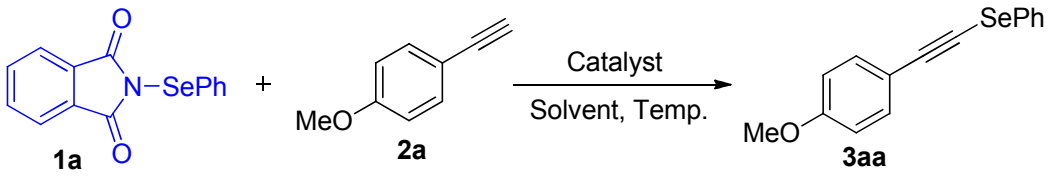


Scheme 2. C-Se cross coupling reactions using various metal catalysts.



Scheme 3. Mechanistic proposal for Ag(I)-catalyzed C-Se bond formation.

388 **Table 1.**Standardization of reaction parameters for phenylselenylation of alkynes.[a]



Entry	Catalyst (mol%)	Base	Solv.	Time (h)	T (°C)	Yield (%)[b]
1	Ag_2CO_3(10)		THF	12	25	0
2	Ag_2CO_3 (10)		THF	12	66	95
3	Ag_2CO_3 (5)		THF	12	66	72
4	Ag_2CO_3 (10)		THF	10	66	78
5	Ag_2CO_3 (10)		NMP	12	100	62
6	Ag_2CO_3 (10)		PhMe	12	100	43
7	$AgNO_3$ (20)		THF	12	66	85
8	AgOTf (20)	K_2CO_3	THF	12	66	95
9	CuI (10)	K_2CO_3	THF	12	66	26
10	CuBr (10)	K_2CO_3	THF	12	66	20
11	$Ni(acac)_2$ (10)	K_2CO_3	THF	12	66	0
12	$Ru(PPh_3)_3Cl_2$ (5)	K_2CO_3	THF	12	66	trace
13	$Co(acac)_2$ (10)	K_2CO_3	NMP	12	100	0
14	Fe nps (1 equiv.)	K_2CO_3	THF	12	66	0
15		K_2CO_3	THF	12	66	0

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390 [a] An equimolecular mixture of 4-methoxy phenyl acetylene (0.3 mmol) and *N*-
391 (phenylseleno)phthalimide (0.3 mmol) was subjected to reaction under various reaction
392 conditions. [b] Yields refer to the those of isolated purified product.

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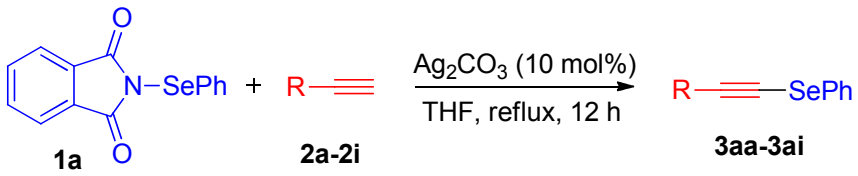
Table 2. Silver catalyzed phenylselenylation of alkynes.



1a **2a-2i** **3aa-3ai**

Entry[a]	Alkyne	Product	Yield (%)[b]
1	**2a**	**3aa**	95
2	**2b**	**3ab**	90
3	**2c**	**3ac**	92
4	**2d**	**3ad**	90
5	**2e**	**3ae**	95
6	**2f**	**3af**	75
7	**2g**	**3ag**	92
8	**2h**	**3ah**	90
9	**2i**	**3ai**	89

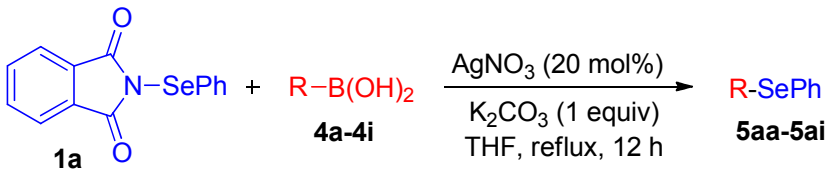
[a]A mixture of alkyne (0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol) and Ag_2CO_3 (10 mol%) was refluxed in dry THF for 12 h. [b]Isolated yields of the products after column purification.

Table 3. Optimization of the reaction conditions for phenylselenylation of organoboronic acid.

Entry[a]	Catalyst (mol%)	Additive	Yield[b] (%)
1	Ag_2CO_3 (10)	-	trace
2	Ag_2CO_3 (10)	K_2CO_3	56
3	Ag_2CO_3 (20)	K_2CO_3	69
4	$AgNO_3$ (10)	K_2CO_3	82
5	$AgNO_3$ (20)	K_2CO_3	96

[a]A mixture of organoboronic acid (4a, 0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol), K_2CO_3 (0.3 mmol) was refluxed in dry THF in the presence of silver catalyst for 12 h. [b] Isolated yields of the product after column purification.

Table 4. C-Se cross coupling of organoboronic acids with NPSP.



Entry[a]	Boronic acid	Product	Yield (%)[b]
1	**4a**	**5aa**	96
2	**4b**	**5ab**	85
3	**4c**	**5ac**	89
4	**4d**	**5ad**	97
5	**4e**	**5ae**	92
6	**4f**	**5af**	90
7	**4g**	**5ag**	93
8	**4h**	**5ah**	80
9	**4i**	**5ai**	74

[a]A mixture of organoboronic acid (0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol), K_2CO_3 (0.3 mmol) and $AgNO_3$ (20 mol%) was refluxed in dry THF for 12 h. [b] Isolated yields of the product after column purification.

Chart 1. The structures of alkynes, alkynyl selenides, boronic acids and diaryl selenides.