



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

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

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## 22 ABSTRACT

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

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

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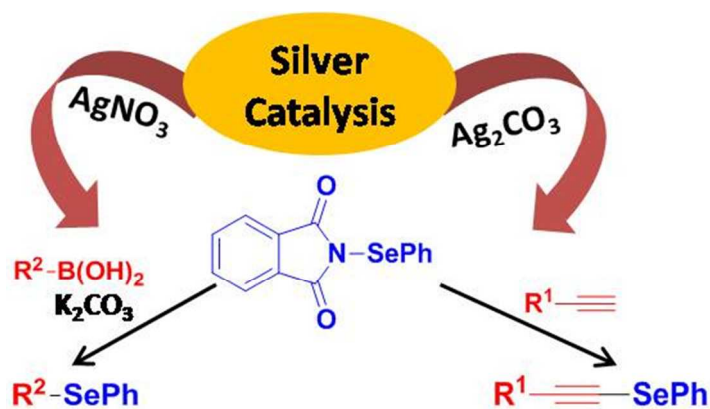
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# Graphical abstract

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

45 Nirmalya Mukherjee,<sup>a</sup> Subhajit Pal,<sup>a</sup> Amit Saha\*<sup>b</sup> and Brindaban C. Ranu\*<sup>a</sup>



## 54 Introduction

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

65 Thus we are interested to investigate selenylation using *N*-(phenylseleno)phthalimide (NPSP) as  
66 the benign source of SePh in presence of a suitable metal catalyst. Palladium, copper and nickel  
67 catalysts being considerably active have been widely used for cross coupling reactions.<sup>18</sup> On the  
68 other hand, among the noble metals silver catalyst is moderately active and has been used for  
69 coupling reaction in a limited way.<sup>19</sup> Earlier, NPSP was involved in the enantioselective  
70 selenylation of aldehydes using different organocatalysts such as L-proline,<sup>20</sup> TMS-protected  
71  $\alpha,\alpha$ -diphenyl-2-pyrrolidinemethanol,<sup>21</sup> and diphenylprolinol silyl ether,<sup>22</sup> enantioselective  
72 selenoactonization using (DHQD)<sub>2</sub>PHAL

73 (1,4-bis[(S)-[(2R,4S,5R)-5-ethylquinuclidin-2-yl]-(6-ethoxy-4-quinoly)methoxy]phthalazine)<sup>23a</sup>  
74 and selenylation of olefins under the catalysis of *p*-TsOH.<sup>23b</sup> As NPSP releases an electrophilic  
75 SePh species we consider it appropriate to involve a nucleophilic coupling partner such as

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

80 **Scheme 1.**

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

86 **Scheme 2.**

## 87 **Results and Discussion**

88 To optimize the reaction conditions a series of experiments were conducted with 4-  
89 methoxyphenylacetylene as a model substrate for selenylation using NPSP in the presence of  
90 Ag(I) catalyst with variation of reaction parameters such as catalyst, solvent, reaction  
91 temperature and time (Table 1). The selenylation was not observed using 10 mol% of Ag<sub>2</sub>CO<sub>3</sub> in  
92 THF at room temperature (25 °C) (Table 1, entry 1). However the increase of reaction  
93 temperature to 66 °C in THF at reflux for 12 h made a remarkable improvement (Table 1, entry  
94 2).

95 **Table 1.**

96 Lowering of catalyst loading to 5 mol% and reducing the reaction time to 10 h decreased the  
97 yield (Table 1, entries 3 and 4). Use of other solvents, *N*-methylpyrrolidinone (NMP) and toluene  
98 at similar conditions did not give better results (Table 1, entries 5 and 6). The involvement of  
99 other silver salts such as AgNO<sub>3</sub> and AgOTf/K<sub>2</sub>CO<sub>3</sub> provided comparable yields (Table 1, entries  
100 7 and 8). For comparison, when Cu-salts are used as catalysts in place of Ag marginal yields (20-  
101 26 %) of products are obtained in addition to considerable amount of dimerized product of  
102 alkyne (Table 1, entries 9 and 10), whereas when other transition metal salts (Ni(acac)<sub>2</sub>,  
103 Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>, Co(acac)<sub>2</sub> and iron nanoparticles) were used no reaction was observed in similar  
104 conditions (Table 1, entries, 11, 12, 13 and 14). The reaction did not occur at all in the absence of  
105 Ag<sub>2</sub>CO<sub>3</sub> (Table 1, entry 15). Thus, in a representative experimental procedure, a mixture of 4-  
106 methoxy phenylacetylene (0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (10  
107 mol%) in dry THF (5 ml) was heated at reflux under argon atmosphere for 12 h. The progress of  
108 the reaction was monitored by TLC. Standard work-up followed by purification through column  
109 chromatography provided the pure product.

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

119

**Table 2.**

120 Being encouraged by the successful selenylation of alkynes using NPSP by this protocol we next  
121 employed organoboronic acids as selenylating counterpart. Interestingly, it was observed that use  
122 of  $\text{Ag}_2\text{CO}_3$  under the same experimental conditions (Table 1) was not effective for boronic acids  
123 (Table 3, entry 1). However, use of 1 equiv. of  $\text{K}_2\text{CO}_3$  along with 10 mol % of  $\text{Ag}_2\text{CO}_3$  improved  
124 the yield of the reaction considerably providing 56% yield of **5aa** (Table 3, entry 2). The increase  
125 of catalyst loading did not improve the yield of the reaction substantially (Table 3, entry 3).  
126 Interestingly, the use of  $\text{AgNO}_3$  (10 mol%) in place of  $\text{Ag}_2\text{CO}_3$  together with 1 equiv. of  $\text{K}_2\text{CO}_3$   
127 in refluxing THF for 12 h produced the diaryl selenide product **5aa** in 82% yield (Table 3, entry  
128 4). However, the best yield was obtained using 20 mol % of  $\text{AgNO}_3$  (Table 3, entry 5).

129

**Table 3.**

130 Thus several organoboronic acids with wide structural variations were subjected to  
131 phenylselenylation with NPSP by the optimized protocol (Table 4, Chart 1). The aryl boronic  
132 acids containing electron donating groups ( $\text{O}^i\text{Pr}$ , Me) participated in the selenylation reaction to  
133 offer the corresponding diaryl selenides in high yields (Table 4, entries 1, 3). The electron-  
134 withdrawing groups ( $\text{OCF}_3$ ,  $\text{NO}_2$ ) in the aryl ring did not affect the yield of products (Table 4,  
135 entries 2, 8). Phenylselenylation was successfully accomplished with bridged substrate like  
136 acenaphthene-5-boronic acid (Table 4, entry 4). The reactions proceeded satisfactorily with  
137 substituted styrenyl boronic acids (Table 4, entries 5, 6) and pentynyl boronic acid (Table 4,  
138 entry 7) without any difficulty. Naphthyl boronic acid also underwent C-Se cross-coupling by  
139 this procedure effectively (Table 4, entry 9).

140

**Table 4.**



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

147 Regarding the reaction pathway of this selenylation process we suggest that NPSP initially  
148 coordinates with Ag<sup>+</sup>, which makes the SePh moiety of NPSP more electrophilic<sup>16,23</sup> (Scheme 3).  
149 It is proposed that silver(I) subsequently activates the terminal alkyne<sup>24</sup> to generate silver  
150 acetylide type intermediate which interacts with activated NPSP producing the alkynyl selenide  
151 product and phthalimide. Ag<sup>+</sup> ion is released in the process and it participates in the next  
152 catalytic cycle. In case of organoboronic acid, a base (K<sub>2</sub>CO<sub>3</sub>) is required to complete the octet of  
153 boron atom in boronic acid so that aryl moiety is able to migrate with its bond pair of electrons<sup>25</sup>  
154 and it reacts with electrophilic SePh leading to the formation of the diaryl selenide product.

### 155 **Scheme 3.**

156 AgNO<sub>3</sub>, having higher effective Lewis acidic activity compared to Ag<sub>2</sub>CO<sub>3</sub>, works more  
157 efficiently in case of C-Se cross-coupling with organoboronic acids.<sup>19e</sup> However, in case of  
158 alkyne, the formation of silver-acetylide type intermediate through the interaction of Ag<sup>+</sup> ion and  
159 terminal alkyne is realized with comparable efficacy with both the salts, AgNO<sub>3</sub> and Ag<sub>2</sub>CO<sub>3</sub>.  
160 Marginally higher activity of Ag<sub>2</sub>CO<sub>3</sub> may be attributed to the higher basicity of CO<sub>3</sub><sup>2-</sup> in  
161 comparison to NO<sub>3</sub><sup>-</sup>.

### 162 **Conclusion**

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

## 170 **Experimental**

### 171 **General**

172 NMR spectra were recorded at 300, 400 and 500 MHz for  $^1\text{H}$  and 75, 100 and 125 MHz for  $^{13}\text{C}$   
173 spectra in  $\text{CDCl}_3$  solutions. Elemental analyses were done at our Institute with an autoanalyzer.  
174  $\text{Ag}_2\text{CO}_3$ ,  $\text{AgNO}_3$ , *N*-(phenylseleno)phthalimide,  $\text{K}_2\text{CO}_3$ , all acetylenes, and boronic acids were  
175 procured commercially.

### 176 **Representative experimental procedure for the cross-coupling of 4-ethynylanisole and *N*- 177 (phenylseleno)phthalimide (Table 2, 3aa)**

178 A mixture of 4-ethynylanisole (40 mg, 0.3 mmol), *N*-(phenylseleno)phthalimide (60 mg, 0.3  
179 mmol),  $\text{Ag}_2\text{CO}_3$  (8.2 mg, 0.03 mmol) in THF (3 mL) was heated at reflux under argon for 12 h  
180 (TLC). The reaction mixture was then allowed to cool and was extracted with diethyl ether (3 x  
181 20 mL). The extract was washed with water (10 mL) and brine (10 mL). Then the organic phase  
182 was dried over  $\text{Na}_2\text{SO}_4$  and evaporated to leave the crude product, which was purified by column  
183 chromatography over silica gel (hexane/diethyl ether 98:2) to provide the pure ((4-  
184 methoxyphenyl)ethynyl)(phenyl)sene as yellow gummy liquid, (82 mg, 95%); IR

185 (neat):  $\nu = 3306, 3140, 3007, 2925, 2851, 2316, 2150, 1595, 1575, 1511, 1470, 1452, 1398, 129$   
186  $6, 1255, 1161 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.82 (s, 3H), 6.87 (dd,  $J_1 = 2 \text{ Hz}, J_2 = 6.5 \text{ Hz}$ ,  
187 2H), 7.27-7.34 (m, 3H), 7.46 (dd,  $J_1 = 2 \text{ Hz}, J_2 = 7 \text{ Hz}$ , 2H), 7.58 (dd,  $J_1 = 1 \text{ Hz}, J_2 = 8.5 \text{ Hz}$ , 2H)  
188 ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  55.4, 67.3, 114.1, 115.4, 127.1, 129.0, 129.4, 129.6, 133.7,  
189 160.1 ppm; anal. calcd. for  $\text{C}_{15}\text{H}_{12}\text{OSe}$ ; C 62.73, H 4.21; found: C 62.77, H 4.28 %.

190 This procedure was followed for all the reactions listed in Table 2 and Table 4. Although the  
191 representative procedure is based on mmol scale reaction scaling up to 10 mmol also produced  
192 similar results. All of the known compounds are identified by their spectroscopic data ( $^1\text{H NMR}$   
193 and  $^{13}\text{C NMR}$ ) and the data are consistent with those reported earlier. Similarly all of the  
194 unknown compounds are well characterized by their spectroscopic and spectrometric data (IR,  
195  $^1\text{H NMR}$ ,  $^{13}\text{C NMR}$  and elemental analysis). All these data are provided in below.

196 **((2-Methoxyphenyl)ethynyl)(phenyl)selane (Table 2, 3ab)**: Yellow viscous liquid, 90%, 77.54  
197 mg, IR (neat):  $\nu = 3061, 3019, 2160, 1589, 1472, 1425, 1263, 1213 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  
198  $\text{CDCl}_3$ ):  $\delta$  3.90 (s, 3H), 6.88-6.93 (m, 2H), 7.25-7.33 (m, 4H), 7.60 (d,  $J = 7.5 \text{ Hz}$ , 1H), 7.64 (dd,  
199  $J = 1.5 \text{ Hz}, 8.7 \text{ Hz}$ , 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  55.9, 72.9, 99.8, 110.8, 112.6,  
200 120.5, 126.9, 128.8, 129.5, 130.0, 130.4, 133.5, 134.3, 160.4 ppm; anal. calcd. for  $\text{C}_{15}\text{H}_{12}\text{OSe}$ ; C  
201 62.73, H 4.21; found: C 62.75, H 4.26 %.

202 **((3-Fluorophenyl)ethynyl)(phenyl)selane<sup>7d</sup> (Table 2, 3ac)**: Viscous liquid, 92%, 75.94 mg,  $^1\text{H}$   
203 NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.93-6.97 (m, 1H), 7.09 (dd,  $J = 1.5 \text{ Hz}, J = 9.5 \text{ Hz}$ , 1H), 7.16-7.21  
204 (m, 3H), 7.22-7.27 (m, 2H), 7.49-7.51 (m, 2H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  71.1, 101.6  
205 (d,  $J_{\text{C-F}} = 3 \text{ Hz}$ ), 115.9 (d,  $J_{\text{C-F}} = 21 \text{ Hz}$ ), 118.5 (d,  $J_{\text{C-F}} = 23 \text{ Hz}$ ), 125.1 (d,  $J_{\text{C-F}} = 9 \text{ Hz}$ ), 127.4,  
206 127.6 (d,  $J_{\text{C-F}} = 3 \text{ Hz}$ ), 128.6, 129.4, 129.7, 130.0, 130.1, 162.4 (d,  $J_{\text{C-F}} = 245 \text{ Hz}$ ) ppm.

207 **Phenyl((2-(trifluoromethyl)phenyl)ethynyl)selane (Table 2, 3ad):** Colourless gummy liquid,  
208 90%, 87.79 mg; IR (neat):  $\nu = 3129, 2925, 2161, 1615, 1585, 1480, 1429, 1388, 1316, 1265,$   
209  $1171, 1130 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27-7.30 (m, 1H), 7.34 (t,  $J = 7.5 \text{ Hz}$ , 2H),  
210 7.40 (t,  $J = 7.5 \text{ Hz}$ , 1H), 7.50 (t,  $J = 7.5 \text{ Hz}$ , 1H), 7.61 (d,  $J = 7.5 \text{ Hz}$ , 3H), 7.66 (d,  $J = 8 \text{ Hz}$ , 1H)  
211 ppm;  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  76.4, 98.9, 121.5 (d,  $J = 2 \text{ Hz}$ ), 122.3, 125, 126 (q,  $J = 5$   
212 Hz), 127.4, 128, 128.5, 129.5 (q,  $J = 7 \text{ Hz}$ ), 131, 131.4 (d,  $J = 17 \text{ Hz}$ ), 133.9 ppm; anal. calcd. for  
213  $\text{C}_{15}\text{H}_9\text{F}_3\text{Se}$ ; C 55.40, H 2.79; found: C 55.37, H 2.77 %.

214 **(6-Methoxynaphthalen-2-yl)(phenyl)selane<sup>7d</sup> (Table 2, 3ae):** Colourless gummy liquid, 95%,  
215 89.26 mg,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.92 (s, 3H), 7.10-7.18 (m, 2H), 7.27-7.34 (m, 3H),  
216 7.51 (dd,  $J_1 = 1.5\text{Hz}$ ,  $J_2 = 8.4\text{Hz}$ , 1H), 7.60-7.71 (m, 4H), 7.95(s, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  
217  $\text{CDCl}_3$ ):  $\delta$  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,  
218 129.7, 131.8, 134.5, 158.6 ppm.

219 **3-((Phenylselanyl)ethynyl)thiophene (Table 2, 3af):** Colourless gummy liquid, 75%, 59 mg;  
220 IR (neat):  $\nu = 3306, 3119, 2925, 2851, 1636, 1575, 1480, 1399, 1316, 1120 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300  
221 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18 (dd,  $J_1 = 5.1$ ,  $J_2 = 0.9 \text{ Hz}$ , 1H), 7.26-7.36 (m, 4H), 7.53-7.59 (m, 3H) ppm;  
222  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  68.9, 97.9, 116.3, 122.4, 125.4, 127.2, 129.0, 129.2, 129.7, 129.9,  
223 130.2 ppm; anal. calcd. for  $\text{C}_{12}\text{H}_8\text{SSe}$ ; C 54.76, H 3.06; found: C 54.78, H 3.03 %.

224 **(Cyclohexylethynyl)(phenyl)selane (Table 2, 3ag):** Yellow gummy liquid, 92%, 72.6 mg; IR  
225 (neat):  $\nu = 3305, 3140, 2935, 2851, 1636, 1575, 1480, 1440, 1399, 1109, 1007 \text{ cm}^{-1}$ ;  $^1\text{H NMR}$   
226 (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.23-1.26 (m, 3H), 1.42-1.48 (m, 3H), 1.64-1.68 (m, 2H), 1.77-1.80 (m,  
227 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;  $^{13}\text{C NMR}$

228 (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.9, 25.9, 30.4, 31.0, 32.8, 57.5, 109.0, 126.7, 128.5, 128.6, 129.4, 129.7  
229 ppm; anal. calcd. for  $\text{C}_{14}\text{H}_{16}\text{Se}$ ; C 63.88, H 6.13; found: C 63.82, H 6.17 %.

230 **Ethyl 3-(phenylselanyl)propiolate (Table 2, 3ah):** Yellow gummy liquid, 90%, 68.35 mg; IR  
231 (neat):  $\nu = 3398, 3305, 3129, 2976, 2925, 2851, 2150, 1697, 1575, 1480, 1441, 1392, 1368, 1245,$   
232  $1099, 1017, \text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.32 (t,  $J = 5.6\text{Hz}$ , 3H), 4.25 (q,  $J = 5.6\text{Hz}$ ,  
233 2H), 7.30-7.37 (m, 3H), 7.59 (dd,  $J_1 = 1.2\text{Hz}$ ,  $J_2 = 6.4\text{Hz}$ , 2H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  
234 14.2, 62.1, 74.9, 96.4, 116.2, 126.2, 128.3, 130.0, 130.3, 152.80 ppm; anal. calcd. for  $\text{C}_{11}\text{H}_{10}\text{OSe}$ ;  
235 C 52.19, H 3.98; found: C 52.23, H 3.94 %.

236 **((4-Phenoxyphenyl)ethynyl)(phenyl)selane (Table 2, 3ai):** Yellow gummy liquid, 89%, 93.2  
237 mg; IR (neat):  $\nu = 3295, 3140, 2925, 2851, 2150, 1570, 1490, 1429, 1388, 1245, 1192, 1151,$   
238  $1109, 1017, 872 \text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.95 (dd,  $J_1 = 9, J_2 = 2.5 \text{Hz}$ , 2H), 7.04 (d,  
239  $J = 8 \text{Hz}$ , 2H), 7.15 (t,  $J = 7.5 \text{Hz}$ , 1H), 7.25-7.28 (m, 1H), 7.32-7.39 (m, 4H), 7.46-7.49 (m, 2H),  
240 7.57-7.60 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  68.4, 102.6, 117.8, 118.4, 119.6, 124.1,  
241 127.2, 129.1, 129.2, 129.6, 130.0, 133.7, 156.4, 158.1 ppm; anal. calcd. for  $\text{C}_{20}\text{H}_{14}\text{OSe}$ ; C 68.77,  
242 H 4.04; found: C 68.73, H 4.08 %.

243 **(3-Isopropoxyphenyl)(phenyl)selane (Table 4, 5aa):** Yellow gummy liquid, 96%, 83.8 mg; IR  
244 (neat):  $\nu = 3140, 2976, 2935, 2851, 1718, 1585, 1480, 1440, 1378, 1276, 1245, 1171, 1120, 1017,$   
245  $946 \text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.34 (d,  $J = 6\text{Hz}$ , 6H), 4.54 (m, 1H), 6.83 (dd,  $J_1 = 2$   
246  $\text{Hz}$ ,  $J_2 = 6.5 \text{Hz}$ , 2H), 7.19-7.22 (m, 3H), 7.33-7.35 (m, 2H), 7.48 (dd,  $J = 2\text{Hz}$ ,  $J = 6.5 \text{Hz}$ , 2H)  
247 ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.0, 22.1, 70.1, 76.85, 117.0, 119.7, 126.5, 129.27, 131.1,  
248 133.39, 136.6, 138.3, 158.3 ppm; anal. calcd. for  $\text{C}_{15}\text{H}_{16}\text{OSe}$ ; C 61.86, H 5.54; found: C 61.44, H  
249 5.14 %.

250 **Phenyl(4-(trifluoromethoxy)phenyl)selane (Table 4, 5ab):** Yellow gummy liquid, 85%, 80.9  
251 mg; IR (neat):  $\nu = 3130, 2915, 1636, 1398, 1181, 1110, 987, 760 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  
252  $\text{CDCl}_3$ ):  $\delta$  7.11 (dd,  $J_1 = 1.2 \text{ Hz}$ ,  $J_2 = 9 \text{ Hz}$ , 2H), 7.28-7.33 (m, 3H), 7.43-7.51(m, 4H) ppm;  $^{13}\text{C}$   
253 NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  121.9, 122.2, 128.0, 129.6, 130.0, 130.4, 133.6, 134.0, 148.6 ppm;  
254 anal. calcd. for  $\text{C}_{13}\text{H}_9\text{F}_3\text{OSe}$ ; C 49.23, H 2.86; found: C 49.27, H 2.88 %.

255 **Phenyl(*o*-tolyl)selane<sup>26</sup> (Table 4, 5ac):** Yellow liquid, 89%, 66 mg;  $^1\text{H}$  NMR (500 MHz,  
256  $\text{CDCl}_3$ ):  $\delta$  2.46 (s, 3H), 7.10-7.13 (m, 1H), 7.23-7.39 (m,5H), 7.40-7.46 (m, 1H) ppm;  $^{13}\text{C}$  NMR  
257 (100 MHz,  $\text{CDCl}_3$ ): 22.4, 126.8, 127.2, 127.9, 129.4, 130.3, 130.9, 131.8, 132.8, 133.8, 140.0  
258 ppm.

259 **(1,2-Dihydroacenaphthylen-5-yl)(phenyl)selane (Table 4, 5ad):** Colourless gummy liquid,  
260 97%, 90 mg; IR (neat):  $\nu = 3110, 2815, 1436, 1371, 1281, 1141 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  
261  $\text{CDCl}_3$ ):  $\delta$  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-  
262 7.44 (m, 1H), 7.76 (dd,  $J_1 = 5.6 \text{ Hz}$ ,  $J_2 = 24 \text{ Hz}$ , 2H) ppm;  $^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.2,  
263 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  
264 ppm; anal. calcd. for  $\text{C}_{18}\text{H}_{14}\text{Se}$ ; C 69.91, H 4.56; found: C 69.27, H 4.48 %.

265 **(*E*)-(4-Methylstyryl)(phenyl)selane<sup>7b</sup> (Table 4, 5ae):** Yellow gummy liquid, 92%, 75.4 mg;  $^1\text{H}$   
266 NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.33 (s, 3H), 6.89 (dd,  $J_1 = 4 \text{ Hz}$ ,  $J_2 = 15.5 \text{ Hz}$ , 1H), 7.10-7.14 (m,  
267 3H), 7.23-7.33 (m, 5H), 7.53-7.55 (m, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 117.9,  
268 126.1, 127.4, 129.4, 129.5, 130.6, 132.4, 134.4, 135.8, 137.7 ppm.

269 **(*E*)-(4-Methoxystyryl)(phenyl)selane<sup>7a</sup> (Table 4, 5af):** Yellow gummy liquid, 90%, 78.1 mg;  
270  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.81 (s, 3H), 6.85-6.91 (m, 3H), 7.02 (d,  $J = 15.6 \text{ Hz}$ , 1H), 7.25-

271 7.31 (m, 5H), 7.52-7.55 (m, 2H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  55.4, 114.2, 116.0, 127.2,  
272 127.5, 129.4, 130.0, 130.9, 132.1, 136.0, 159.5 ppm.

273 **Pent-1-yn-1-yl(phenyl)selane**<sup>27</sup> (Table 4, 5ag): Yellow gummy liquid, 93%, 63 mg;  $^1\text{H}$  NMR  
274 (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.06 (t,  $J = 7.6$  Hz, 3H), 1.65 (sextet,  $J = 7.2$  Hz, 2H), 2.46 (t,  $J = 7.2$  Hz,  
275 2H), 7.23-7.34 (m, 3H), 7.53-7.55 (m, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 22.3, 22.7,  
276 57.7, 76.8, 104.6, 126.8, 128.7, 129.5 ppm.

277 **(3-Nitrophenyl)(phenyl)selane**<sup>12b</sup> (Table 4, 5ah): Yellow gummy liquid, 80%, 66.7 mg;  $^1\text{H}$   
278 NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36-7.41(m, 4H), 7.56-7.59 (m, 2H), 7.63-7.66 (m, 1H), 8.03-8.06  
279 (m, 1H), 8.20 (t,  $J = 2.1$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  121.7, 125.9, 128.6, 128.9,  
280 129.9, 130.0, 134.9, 137.1, 148.8 ppm.

281 **Naphthalen-2-yl(phenyl)selane**<sup>7b</sup> (Table 4, 5ai): Yellow gummy liquid, 74%, 62.9 mg,  $^1\text{H}$   
282 NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27 (dd,  $J_1 = 6.3$  Hz,  $J_2 = 3.3$  Hz, 3H), 7.44-7.54 (m, 5H), 7.73 (d,  $J$   
283 = 7.8 Hz, 2H), 7.78-7.82 (m, 1H), 7.99 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  126.3,  
284 126.6, 127.5, 127.9, 128.6, 128.9, 129.5, 130.6, 131.3, 132.2, 132.6, 133.0, 134.1 ppm.

## 285 Supplementary Material

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

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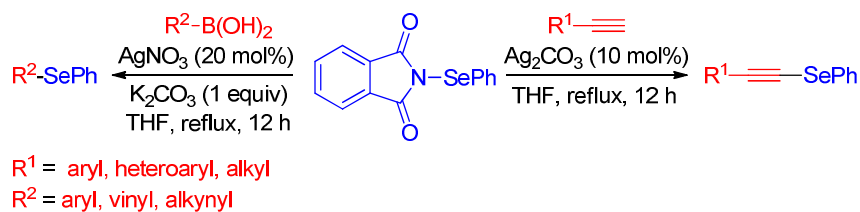
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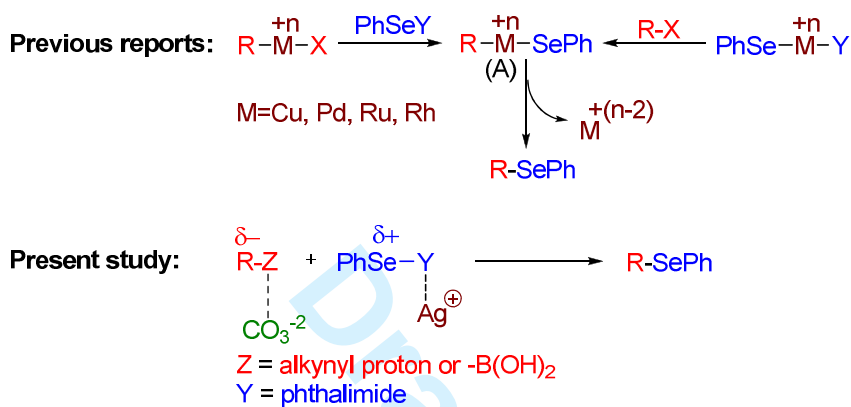
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379

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

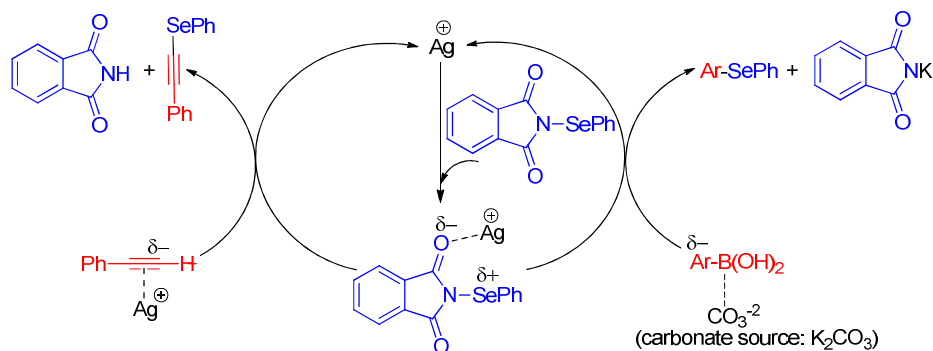
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383 **Scheme 2.** C-Se cross coupling reactions using various metal catalysts.

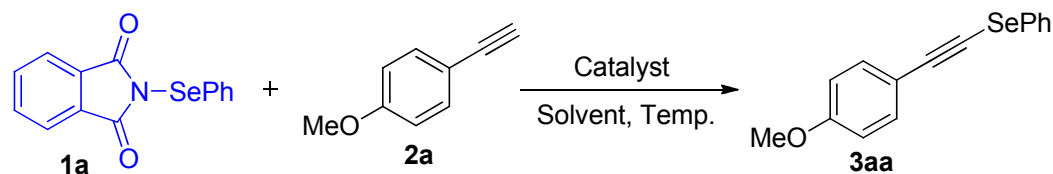
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386 **Scheme 3.** Mechanistic proposal for Ag(I)-catalyzed C-Se bond formation.

387

388 **Table 1.** Standardization of reaction parameters for phenylselenylation of alkynes.<sup>a</sup>

Entry	Catalyst (mol%)	Base	Solv.	Time (h)	T (°C)	Yield (%) <sup>b</sup>
1	Ag <sub>2</sub> CO <sub>3</sub> (10)		THF	12	25	0
2	Ag <sub>2</sub> CO <sub>3</sub> (10)		THF	12	66	95
3	Ag <sub>2</sub> CO <sub>3</sub> (5)		THF	12	66	72
4	Ag <sub>2</sub> CO <sub>3</sub> (10)		THF	10	66	78
5	Ag <sub>2</sub> CO <sub>3</sub> (10)		NMP	12	100	62
6	Ag <sub>2</sub> CO <sub>3</sub> (10)		PhMe	12	100	43
7	AgNO <sub>3</sub> (20)		THF	12	66	85
8	AgOTf (20)	K <sub>2</sub> CO <sub>3</sub>	THF	12	66	95
9	CuI (10)	K <sub>2</sub> CO <sub>3</sub>	THF	12	66	26
10	CuBr (10)	K <sub>2</sub> CO <sub>3</sub>	THF	12	66	20
11	Ni(acac) <sub>2</sub> (10)	K <sub>2</sub> CO <sub>3</sub>	THF	12	66	0
12	Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub> (5)	K <sub>2</sub> CO <sub>3</sub>	THF	12	66	trace
13	Co(acac) <sub>2</sub> (10)	K <sub>2</sub> CO <sub>3</sub>	NMP	12	100	0
14	Fe nps (1 equiv.)	K <sub>2</sub> CO <sub>3</sub>	THF	12	66	0
15		K <sub>2</sub> CO <sub>3</sub>	THF	12	66	0

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390 <sup>a</sup> 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. <sup>b</sup> Yields refer to the those of isolated purified product.

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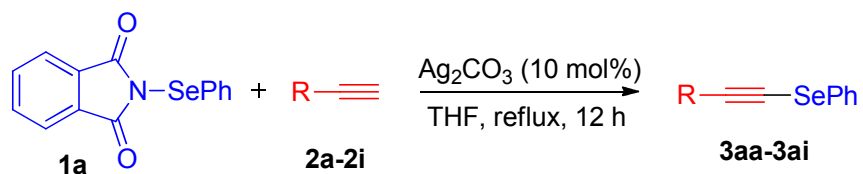
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398 **Table 2.** Silver catalyzed phenylselenylation of alkynes.



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

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400 <sup>a</sup>A mixture of alkyne (0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (10  
 401 mol%) was refluxed in dry THF for 12 h. <sup>b</sup>Isolated yields of the products after column  
 402 purification.

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

Entry <sup>a</sup>	Catalyst (mol%)	Additive	Yield <sup>b</sup> (%)
1	Ag <sub>2</sub> CO <sub>3</sub> (10)	-	trace
2	Ag <sub>2</sub> CO <sub>3</sub> (10)	K <sub>2</sub> CO <sub>3</sub>	56
3	Ag <sub>2</sub> CO <sub>3</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	69
4	AgNO <sub>3</sub> (10)	K <sub>2</sub> CO <sub>3</sub>	82
5	AgNO <sub>3</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	96

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409 <sup>a</sup>A mixture of organoboronic acid (4a, 0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol),410 K<sub>2</sub>CO<sub>3</sub> (0.3 mmol) was refluxed in dry THF in the presence of silver catalyst for 12 h. <sup>b</sup>

411 Isolated yields of the product after column purification.

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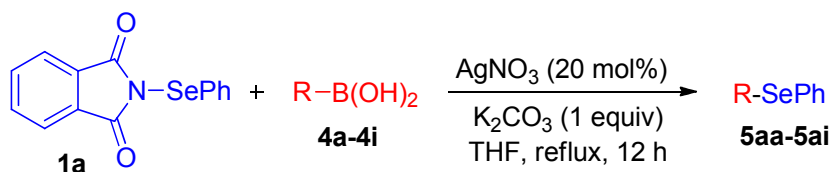
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423 **Table 4.** C-Se cross coupling of organoboronic acids with NPSP.

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

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425 <sup>a</sup>A mixture of organoboronic acid (0.3 mmol), *N*-(phenylseleno)phthalimide (0.3 mmol),  
 426  $\text{K}_2\text{CO}_3$  (0.3 mmol) and  $\text{AgNO}_3$  (20 mol%) was refluxed in dry THF for 12 h. <sup>b</sup> Isolated  
 427 yields of the product after column purification.

428

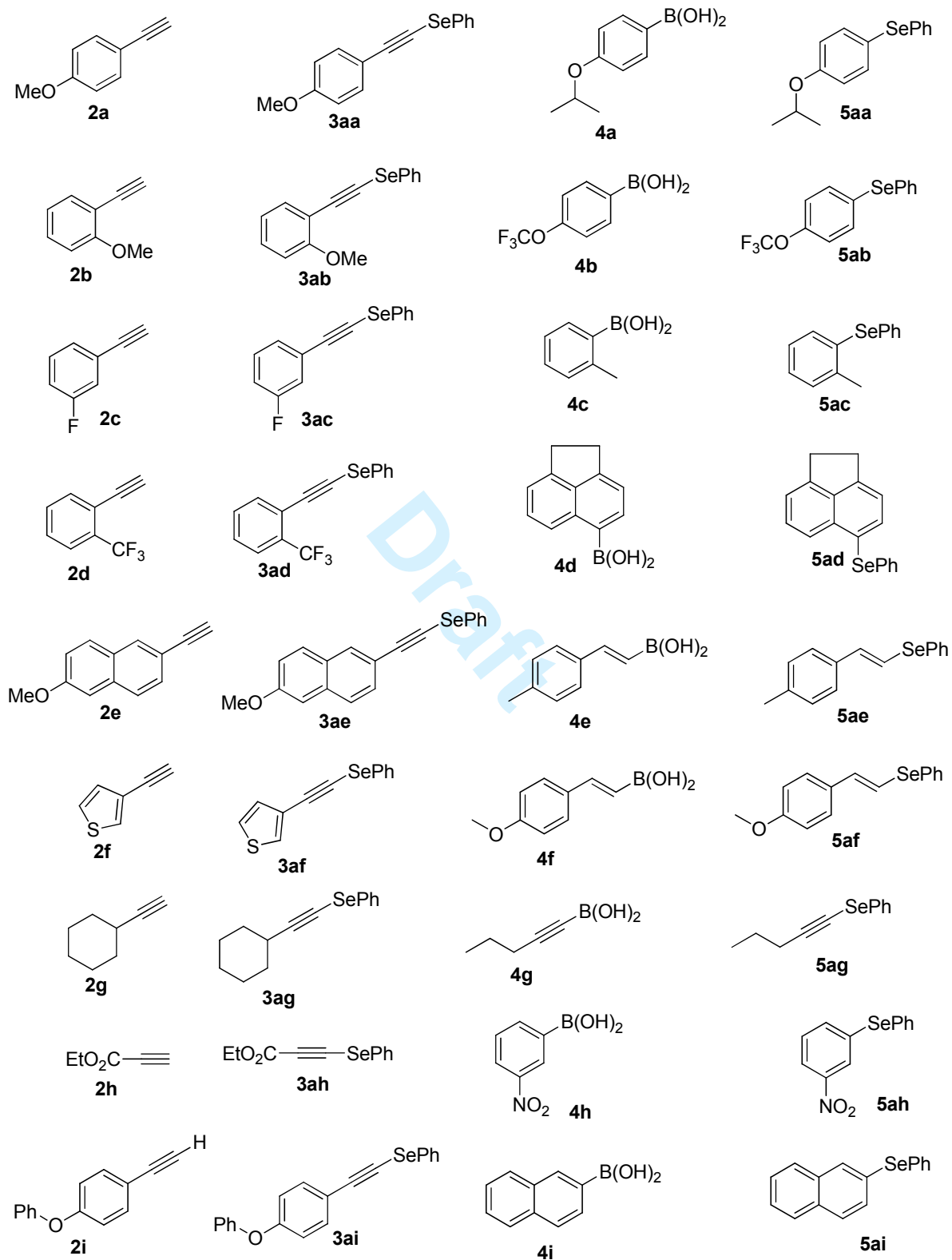
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431



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



433