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# Copper-catalyzed C–Se coupling of diphenyl diselenide with arylboronic acids at room temperature

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ABSTRACT

An efficient synthetic protocol for the Cu-catalyzed cross-coupling of diphenyl diselenide and arylboronic acid at room temperature was described. This catalytic system could tolerate a variety of arylboronic acids with only 3 mol % amount of $CuSO_4$ as the catalyst and inexpensive 1,10-phen. $H_2O$ as the ligand. Moreover, this catalytic system used environment-friendly EtOH as the solvent and catalytic amount of $Na_2CO_3$ (20 mol %) as the base in the air.



## 1. Introduction

Selenium is one of the essential trace elements, which has a variety of immune and biological functions, especially in the prevention of cardiovascular disease, anti-tumor, anti-viral diseases, as well as anti-aging effect.[1] In addition, many organoselenium compounds have been studied as catalysts and intermediates in organic synthesis[2] and material science.[3] Therefore, it is very significant to research on a variety of synthetic methods for organoselenium. The traditional methods for the formation of C–Se bond are associated with serious disadvantages including: (i) the use of toxic solvents, such as hexamethyl phosphoric triamide (HMPA);[4] (ii) harsh reaction conditions, such as reaction of benzeneselenate anion and aryl halide in liquid ammonia under UV light, etc.;[5] (iii) expensive and toxic reagents.[6] To resolve these problems, many research groups have made great effort to develop a number of synthesis methods in recent years. Transition-metal-catalyzed methods played an important role in C–Se bond formation. A variety of metals, including Ni,[7] Pd,[8] In,[9,13] Zn[10] Cu,[11] and Fe[14] catalyst systems have been studied for this purpose. However, the application of Pd catalyst is restricted in large-scale processes because of their high cost, air sensitivity and of 10 tedious procedure for the preparation of ligands, and the scope of Cu and other transition-metal catalytic systems needed high reaction temperature or aprotic solvent. So it is important that more mild (at room temperature), efficient, and environment-friendly catalytic system need to be developed.

With the wide variety of commercially available and stable boronic acids and derivatives, many studies have reported boronic acids as reagents for the C–Se bond formation. In the past years, the reactions of organoboronic acids with diselenides have been reported. The first C–Se cross-coupling reaction of boronic acids with diselenides was reported by Taniguchi[12a] using CuI as catalyst at 100 °C in DMSO–$H_2O$ mixed solvent (Scheme 1a). Later, Wang et al. described that indium[13] (Scheme 1b) or iron[14] (Scheme 1c) catalyzed cross-coupling reactions of arylboronic acids with diselenides employing DMSO as solvent at 130 °C. Alves et al. also reported the reaction of diaryl diselenides and arylboronic acids, which used a recyclable catalyst[15] (Scheme 1d) or a recyclable solvent[16] (Scheme 1e). Unfortunately, these reactions have some disadvantages, such as high reaction temperature, harmful solvents, and long reaction time. Recently, our group[17] reported the oxidative cross-coupling reactions of diverse boronic acids with thiols using $CuSO_4$ as a simple and inexpensive catalyst in ethyl alcohol at room temperature (Scheme 2). We would like to develop a general protocol for the cross-coupling reactions of diverse boronic acids with diphenyl diselenide with a simple copper catalyst in an environment-friendly solvent at room temperature.

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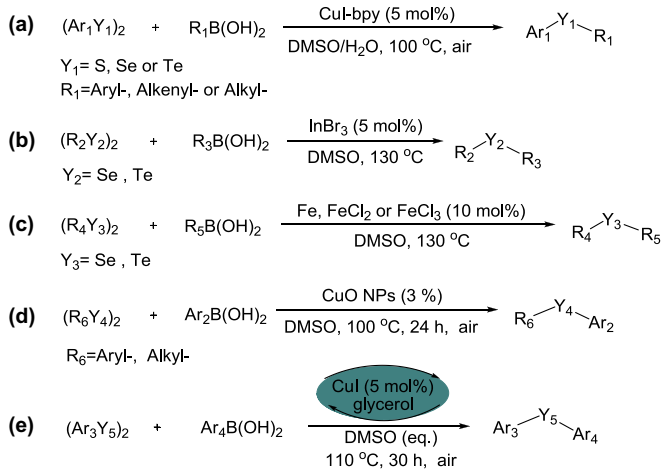
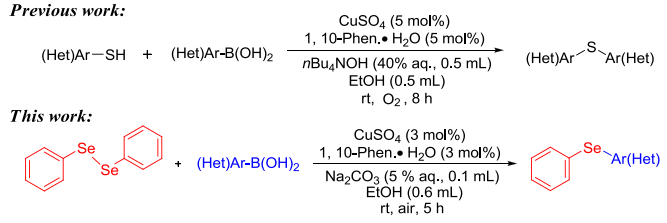



**Scheme 1.** The reported reactions of boronic acids with diselenides.



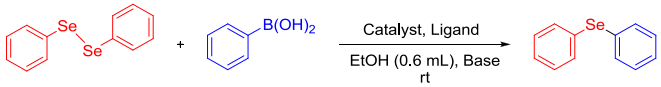

**Scheme 2.** Our studies on the reactions of boronic acids with chalcogenide.

## 2. Results and discussion

The reaction of diphenyl diselenide and phenylboronic acid was carried out as a model reaction (Table 1). According to our developed method,[17] the initial study was carried out using $CuSO_4$ as a catalyst and tetra-*n*-butylammonium hydroxide ($^nBu_4NOH$ (40% aq)) as a base in EtOH under $O_2$ atmosphere at room temperature, 98% yield of product was obtained (Table 1, entry 1). Because $^nBu_4NOH$ (40% aq) is relatively expensive and strongly alkaline, we attempted to use traditional inorganic bases, such as KOH, NaOH, $Cs_2CO_3$, $Na_2CO_3$ instead of $^nBu_4NOH$ (40% aq) (Table 1, entries 2–5). To our delight, the yield reached up to 98% when KOH (5% aq) (Table 1, entry 2) or $Na_2CO_3$ (5% aq) (Table 1, entry 5) was used. We chose $Na_2CO_3$ as a base in further examination. Then, we screened the concentration of $Na_2CO_3$ and investigated the influence of the amount of $Na_2CO_3$ on this reaction (Table 1, entries 6–9). The results showed that 0.1 mL of 5% $Na_2CO_3$ (aq) was suitable for the desired conversion (Table 1, entry 8). To make this reaction system simpler, we carried out this reaction in the air, and the yield could reach 85% (Table 1, entry 10). To our pleasure, a 99% yield was observed when the amount of phenylboronic acid is increased to 1.1 equiv (with comparison of 0.5 equiv of diphenyl diselenide) (Table 1, entry 11). The yield decreased sharply to 50% when the reaction time reduced to 3 h under air atmosphere (Table 1, entry 12). It could not provide satisfactory results using water as a solvent instead of EtOH (Table 1, entry 13). Considering the influence of catalyst, when we used other copper salts as catalyst, the product yield could reach up to 75%–80% (Table 1, entries 14 and 15). Only 17% product was observed when the reaction was performed in the presence of $FeCl_3 \cdot 3H_2O$ (Table 1, entry 16), and no product was obtained without the catalyst (Table 1, entry 18). The control experiment showed that only a 25% yield of product was observed in the absence of a ligand (Table 1, entry 19).

With the optimal condition in hand, we examined the isolated yields for the reactions of a number of boronic acids and diphenyl diselenide. The results are listed in Table 2. It was found that *o*-methyl, *m*-methyl, *p*-methyl groups on the phenylboronic acids rings were very effective in this process and gave the desired products over 93% yields (Table 2, entries **1b**–**d**). Furthermore, the bromo, chloro groups did not interfere with the transformation, which made further cross-coupling at the halogenated positions (Table 2, entries **1h**–**j**). Although the reaction yields of 4-bromophenylboronic acid and 4-(trifluoromethyl)phenylboronic acid were a little low for 5 h, they could reach up to 80% and 82% by increasing the reaction time, respectively (Table 2, entries **1j**–**k**). More importantly, the coupling of phenylboronic acid with diselenides in a 10 mmol (gram scale) also

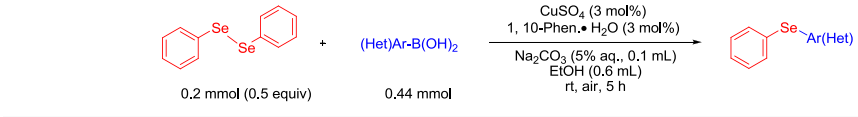
**Table 1**
Optimization of the reaction conditions[a]

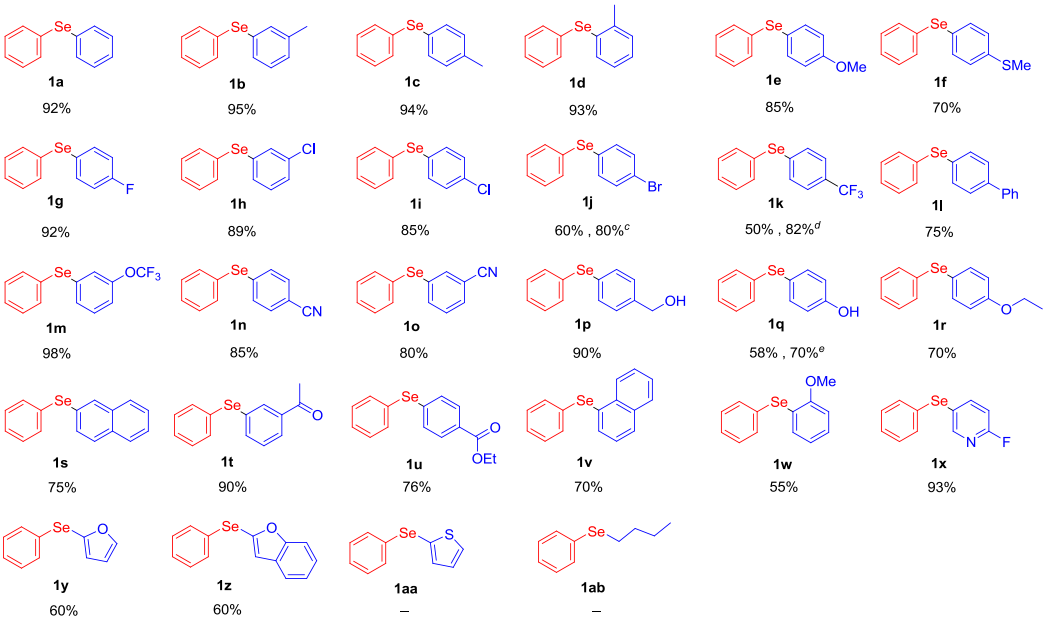



| Entry | Base | Catalyst (mol %) | Ligand (mol %) | Atmosphere | *t* (h) | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | $^nBu_4NOH$ (40% aq, 0.5 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 98 |
| 2 | KOH (5% aq, 0.5 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 98 |
| 3 | NaOH (5% aq, 0.5 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 95 |
| 4 | $Cs_2CO_3$ (5% aq, 0.5 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 72 |
| 5 | $Na_2CO_3$ (5% aq, 0.5 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 98 |
| 6 | $Na_2CO_3$ (1% aq, 0.5 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 59 |
| 7 | $Na_2CO_3$ (5% aq, 0.2 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 83 |
| 8 | $Na_2CO_3$ (5% aq, 0.1 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 98 |
| 9 | — | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | $O_2$ | 5 | 45 |
| 10 | $Na_2CO_3$ (5% aq, 0.1 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | Air | 5 | 85 |
| **11**[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | **$CuSO_4$ (3)** | 1,10-phen. $H_2O$ (3) | **Air** | **5** | **99** |
| 12[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | Air | 3 | 50 |
| 13[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | $CuSO_4$ (3) | 1,10-phen. $H_2O$ (3) | Air | 5 | 35[c] |
| 14[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | $Cu(OAc)_2$ (3) | 1,10-phen. $H_2O$ (3) | Air | 5 | 80 |
| 15[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | CuBr (3) | 1,10-phen. $H_2O$ (3) | Air | 5 | 75 |
| 16[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | $FeCl_3 \cdot 3H_2O$ (3) | 1,10-phen. $H_2O$ (3) | Air | 5 | 17 |
| 17[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | $CuSO_4$ (1) | 1,10-phen. $H_2O$ (1) | Air | 5 | 43 |
| 18[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | — | 1,10-phen. $H_2O$ (3) | Air | 5 | Trace |
| 19[d] | $Na_2CO_3$ (5% aq, 0.1 mL) | $CuSO_4$ (3) | — | Air | 5 | 25 |

The highest yield is indicated in bold.
[a] Unless otherwise noted, 0.2 mmol diphenyl diselenide, 0.4 mmol phenylboronic acid, 0.6 mL EtOH.
[b] Yields determined by GC.
[c] In 0.6 mL $H_2O$.
[d] 0.44 mmol phenylboronic acid.

**Table 2**
The reactions of diphenyl diselenide with arylboronic acids[a,b]



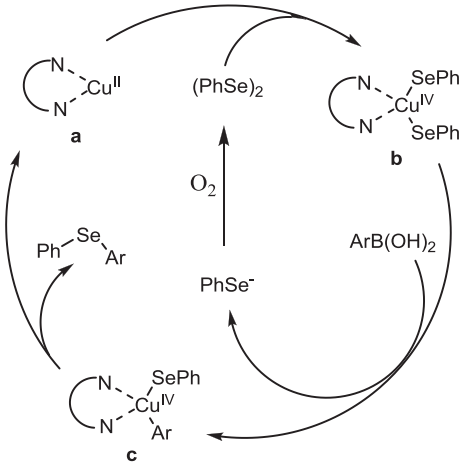




[a] Reactions were carried out using aryl or heteroaryl boronic acids (0.44 mmol), diphenyl diselenide (0.2 mmol) at room temperature under air atmosphere for 5 h. [b] Yields are given for isolated products and are calculated by the standard of diselenides. [c] 17 h. [d] 22 h. [e] $Na_2CO_3$ (5% aq., 1.0 mL), EtOH (1.0 mL).

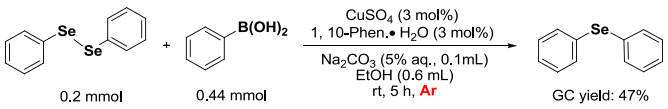
could give 73% isolated yield, which made this protocol suitable for industrial application. To our delight, 4-hydroxyphenolboronic acid was also successfully coupled in good yield avoiding oxidative C–O coupling (Table 2, entry **1q**).

Carbonyl or ester group substituted arylboronic acids could not be tolerated in our previous C–S coupling reaction,[17] but they gave 90% and 76% yield in this reaction system, respectively (Table 2, entries **1t**–**u**). The above results indicated that electron-withdrawing and electron-donating arylboronic acids were not affected. Although the reaction yields were influenced by sterically hindered ortho substituents, they could still reach up to 55%–70% (Table 2, entries **1v**–**w**). It is noteworthy that heteroaryl boronic acids also provided the corresponding products in good yields (Table 2, entries **1x**–**z**), especially 2-fluoropyridine-5-boronic acid could give a 93% yield (Table 2, entry **1x**). However, 2-thiophene boronic acid and *n*-butyl boronic acid could not react in current protocol (Table 2, entries **1aa**–**ab**).

According to the previous studies[12,17] and the above experimental results, we propose the mechanism as follows (Scheme 3). Initially, Cu (II) intermediate **a** is quickly formed by $CuSO_4$ and 1,10-phen. $H_2O$. Then, intermediate **b** is formed from diphenyl diselenide with Cu (II) intermediate **a** via an oxidative addition, $ArB(OH)_2$ reacts with **b** via transmetallation to form intermediate **c** and $[PhSe]^-$, which is then oxidized by $O_2$ to regenerate $[PhSe]_2$. Sequentially, reductive elimination ensues to form the product PhSeAr and Cu (II) intermediate **a** to complete the catalytic cycle. This reaction may occur under Ar atmosphere and only a 47% yield of product was obtained (Scheme 4).




**Scheme 3.** Proposed mechanism.




**Scheme 4.** The reaction of diphenyl diselenide and phenylboronic acid under argon.

## 3. Conclusion

In conclusion, we developed a simple, efficient, economical, and environmentally friendly protocol for the synthesis of diaryl selenides by coupling of arylboronic acid with diphenyl diselenide under mild reaction conditions. This method has the following advantages: (i) at room temperature; (ii) the use of environment-friendly EtOH as solvent; (iii) under air atmosphere; (iv) only 3 mol % $CuSO_4$ as catalyst. Due to the convenient operation and environmental friendliness of this procedure, we hope the developed catalytic method can be applied not only in laboratory but also in large-scale production.

## 4. Experimental section

### 4.1. General procedures for the optimization of the reaction condition

*4.1.1. General procedure A.* Diphenyl diselenide (0.2 mmol), phenylboronic acid (0.4 mmol), $CuSO_4$ (3 mol %), 1,10-phen. $H_2O$ (3 mol %) were thrown into 25 mL oven-dried Schlenk tube. The tube was evacuated and filled with oxygen (this procedure was repeated three times). Then solvent (0.6 mL) was added with a syringe under a counter flow of oxygen. After 1 min, base (0.1–0.5 mL) was added with a syringe under a counter flow of oxygen and the mixture stirred vigorously at room temperature for 5 h. The reaction mixture was then diluted with $Et_2O$, filtered, washed with copious washings ($Et_2O$), biphenyl (0.4 mmol) was added as internal standard. The yield was determined by GC.

*4.1.2. General procedure B.* Diphenyl diselenide (0.2 mmol), phenylboronic acid (0.4 mmol or 0.44 mmol), Cu or Fe sources (1–3 mol %), 1,10-phen. $H_2O$ (1–3 mol %) were thrown into 25 mL oven-dried Schlenk tube. Then solvent (0.6 mL) was added with a syringe. After 1 min, $Na_2CO_3$ (5% aq, 0.1 mL) was added with a syringe and the mixture stirred vigorously at room temperature for 3 h or 5 h. The reaction mixture was then diluted with $Et_2O$, filtered, washed with copious washings ($Et_2O$), biphenyl (0.4 mmol) was added as internal standard. The yield was determined by GC.

### 4.2. Experimental procedures for the reaction of boronic acids and diphenyl diselenide

Diphenyl diselenide (0.2 mmol), boronic acid (0.44 mmol), $CuSO_4$ (3 mol %, 20 mg), 1,10-phen. $H_2O$ (3 mol %, 24 mg) were thrown into 25 mL oven-dried Schlenk tube. Then, EtOH (0.6 mL) was added with a syringe. After 1 min, $Na_2CO_3$ (5% aq) (0.1 mL or 1 mL) was added and the mixture stirred vigorously at room temperature for 5 h–22 h. After completion of the reaction, the reaction mixture was diluted with $Et_2O$, filtered, washed with copious washings ($Et_2O$ or EtOAc), concentrated. The crude product was purified on a short silica gel column (ethyl acetate or petroleum ether).

*4.2.1. Diphenyl-selenide (**1a**).*[15] The reaction of 5 h, purification by column chromatography (petroleum ether), a colorless oil (86 mg, 92% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.48 (m, 4H), 7.28 (m, 6H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 133.0, 131.1, 129.3, 127.3.

*4.2.2. 3-Tolyl-phenyl-selenid (**1b**).*[11b] The reaction of 5 h, purification by column chromatography (petroleum ether), a pale yellow liquid (94 mg, 95% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.49–7.44 (m, 2H), 7.33 (s, 1H), 7.27 (m, 4H), 7.17 (t, $J$=7.6 Hz, 1H), 7.09 (d, $J$=7.6 Hz, 1H), 2.31 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 139.2, 133.8, 132.8, 131.4, 130.7, 130.3, 129.3, 129.3, 128.3, 127.2, 21.3.

*4.2.3. 4-Tolyl-phenyl-selenide (**1c**).*[11b] The reaction of 5 h, purification by column chromatography (petroleum ether), a yellow liquid (93 mg, 94% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.51–7.37 (m, 4H), 7.29–7.20 (m, 4H), 7.12 (d, $J$=7.9 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 137.7, 133.9, 132.0, 131.5, 130.2, 129.2, 127.7, 126.9, 21.2.

*4.2.4. 2-Tolyl-phenyl-selenide (**1d**).*[15] The reaction of 5 h, purification by column chromatography (petroleum ether), a pale yellow liquid (92 mg, 93% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.40 (dd, $J$=6.4, 3.2 Hz, 2H), 7.34 (d, $J$=7.7 Hz, 1H), 7.30–7.17 (m, 5H), 7.07 (t, $J$=7.4 Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 139.9, 133.7, 132.8, 131.7, 130.8, 130.2, 129.4, 127.9, 127.2, 126.7, 22.4.

*4.2.5. 4-Methoxyphenyl-phenyl-selenide (**1e**).*[13] The reaction of 5 h, purification by column chromatography (petroleum ether), a pale yellow liquid (89 mg, 85% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.50 (d, $J$=8.7 Hz, 2H), 7.32 (d, $J$=7.1 Hz, 2H), 7.23–7.14 (m, 3H), 6.85 (d, $J$=8.7 Hz, 2H), 3.80 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 159.8, 136.5, 133.2, 130.9, 129.1, 126.4, 119.9, 115.1, 55.3.

*4.2.6. 4-Methylthiophenyl-phenyl-selenide (**1f**).*[13] The reaction of 5 h, purification by column chromatography (petroleum ether), a pale yellow liquid (78 mg, 70% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.41 (m, 4H), 7.25 (m, 3H), 7.16 (d, $J$=8.3 Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 138.4, 134.1, 132.3, 131.7, 129.3, 127.2, 127.1, 126.7, 15.7.

*4.2.7. 4-Fluorophenyl-phenyl-selenide (**1g**).*[11j] The reaction of 5 h, purification by column chromatography (petroleum ether), a pale yellow liquid (92 mg, 92% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.49 (dd, $J$=8.4, 5.5 Hz, 2H), 7.41 (m, 2H), 7.29–7.22 (m, 3H), 6.99 (t, $J$=8.6 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 163.4, 161.7, 135.7, 135.7, 132.2, 131.7, 129.3, 127.2, 125.2, 116.6, 116.5.

*4.2.8. 3-Chlorophenyl-phenyl-selenide (**1h**).*[11b] The reaction of 5 h, purification by column chromatography (petroleum ether), a colorless oil (95 mg, 89% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.54–7.49 (m, 2H), 7.40 (s, 1H), 7.30 (m, 4H), 7.21 (m, 1H), 7.17 (m, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 134.9, 133.9, 133.5, 131.7, 130.2, 130.1, 129.8, 129.5, 128.0, 127.2.

*4.2.9. 4-Chlorophenyl-phenyl-selenide (**1i**).*[15] The reaction of 5 h, purification by column chromatography (petroleum ether), a colorless oil (91 mg, 85% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.46 (m, 2H), 7.37 (m, 2H), 7.30–7.26 (m, 3H), 7.23 (m, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 134.1, 133.5, 133.2, 130.6, 129.5, 129.4, 127.6.

*4.2.10. 4-Bromophenyl-phenyl-selenide (**1j**).*[15] The reaction of 17 h, purification by column chromatography (petroleum ether), a white solid (100 mg, 80% yield), mp: 33.7–35.0 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.47 (m, 2H), 7.38 (m, 2H), 7.30 (m, 5H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 134.2, 133.3, 132.4, 130.4, 130.4, 129.5, 127.7, 121.5.

*4.2.11. 4-(Trifluoromethyl)phenyl-phenyl-selenide (**1k**).*[11f] The reaction of 22 h, purification by column chromatography (petroleum ether), a colorless oil (99 mg, 82% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.51 (m, 2H), 7.46 (d, $J$=8.6 Hz, 2H), 7.34–7.28 (m, 3H), 7.12 (d, $J$=8.6 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 148.5, 148.5, 133.9, 133.5, 130.3, 129.9, 129.5, 127.8, 121.8, 121.3, 119.5.

*4.2.12. 4-(Phenyl)phenyl-phenyl-selenide (**1l**).*[18] The reaction of 5 h, purification by column chromatography (petroleum ether), a light yellow solid (93 mg, 75% yield), mp: 71.3–72.2 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.56 (d, $J$=7.7 Hz, 2H), 7.51 (m, 6H), 7.43 (t, $J$=7.7 Hz, 2H), 7.34 (t, $J$=7.4 Hz, 1H), 7.32–7.26 (m, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 140.4, 140.3, 133.3, 133.1, 131.1, 130.2, 129.4, 128.8, 128.0, 127.5, 127.4, 127.0.

*4.2.13. 3-(Trifluoromethoxy)phenyl-phenyl-selenide (**1m**).* The reaction of 5 h, purification by column chromatography (petroleum ether), a colorless oil (124 mg, 98% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.53 (m, 2H), 7.31 (m, 4H), 7.26–7.22 (m, 2H), 7.07 (d, $J$=8.1 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 149.5, 134.2, 133.9, 130.2, 129.9, 129.6, 129.3, 128.2, 124.0, 121.2, 119.5, 119.2. HRMS calcd for $C_{13}H_9F_3OSe$ ($M^+$): 317.9771; found: 317.9774.

*4.2.14. 4-Cyanophenyl-phenyl-selenide (**1n**).*[14b] The reaction of 5 h, purification by column chromatography (petroleum ether/ethyl

acetate=50:1), a colorless oil (88 mg, 85% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.60 (m, 2H), 7.46–7.36 (m, 5H), 7.32 (d, $J$=8.4 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 141.0, 135.7, 132.4, 130.2, 129.9, 129.2, 127.4, 118.8, 109.5.

*4.2.15. 3-Cyanophenyl-phenyl-selenide (**1o**).*[18] The reaction of 5 h, purification by column chromatography (petroleum ether/ethyl acetate=50:1), a colorless oil (83 mg, 80% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.58 (m, 2H), 7.55 (m, 2H), 7.48 (d, $J$=7.6 Hz, 1H), 7.40–7.28 (m, 4H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 135.4, 134.7, 134.4, 134.2, 130.2, 129.9, 129.6, 128.8, 128.4, 118.2, 113.4.

*4.2.16. (4-(Phenylselanyl)phenyl)methanol (**1p**).* The reaction of 5 h, purification by column chromatography (petroleum ether/ethyl acetate=5:1), an orange solid (95 mg, 90% yield), mp: 49.7–51.4 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.48–7.43 (m, 4H), 7.26 (m, 5H), 4.66 (s, 2H), 1.75 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 140.1, 133.3, 132.8, 131.1, 130.2, 129.3, 127.9, 127.3, 64.8. HRMS calcd for $C_{13}H_{12}OSe$ ($M^+$): 264.0053; found: 264.0055.

*4.2.17. 4-Hydroxylphenyl-phenyl-selenide (**1q**).*[8] The reaction of 5 h, purification by column chromatography (petroleum ether/ethyl acetate=20:1), a brown liquid (70 mg, 70% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.46 (d, $J$=8.7 Hz, 2H), 7.36–7.32 (m, 2H), 7.27–7.17 (m, 3H), 6.79 (d, $J$=8.7 Hz, 2H), 5.38 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 155.8, 136.72, 133.0, 131.0, 129.2, 126.5, 120.1, 116.6.

*4.2.18. 4-Ethoxyphenyl-phenyl-selenide (**1r**).* The reaction of 5 h, purification by column chromatography (petroleum ether), a yellow liquid (78 mg, 70% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.49 (d, $J$=8.6 Hz, 2H), 7.32 (d, $J$=7.3 Hz, 2H), 7.19 (m, 3H), 6.84 (d, $J$=8.7 Hz, 2H), 4.02 (q, $J$=7.0 Hz, 2H), 1.41 (t, $J$=7.0 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 159.2, 136.6, 133.3, 130.8, 129.1, 126.4, 119.7, 115.6, 63.5, 14.8. HRMS calcd for $C_{14}H_{14}OSe$ ($M^+$): 278.0210; found: 278.0207.

*4.2.19. 2-Naphthyl-phenyl-selenide (**1s**).*[16] The reaction of 5 h, purification by column chromatography (petroleum ether), a light yellow solid (85 mg, 75% yield), mp: 55.2–56.4 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.99 (s, 1H), 7.81 (m, 1H), 7.73 (m, 2H), 7.50 (m, 5H), 7.30–7.26 (m, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 134.0, 132.9, 132.4, 132.1, 131.2, 130.5, 129.4, 128.8, 128.4, 127.8, 127.4, 127.3, 126.5, 126.2.

*4.2.20. 1-(4-(Phenylselanyl)phenyl)ethanone (**1t**).*[15] The reaction of 5 h, purification by column chromatography (petroleum ether/ethyl acetate=20:1), a colorless liquid (99 mg, 90% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 8.02 (t, $J$=1.7 Hz, 1H), 7.84–7.79 (m, 1H), 7.61–7.56 (m, 1H), 7.50 (m, 2H), 7.34 (t, $J$=7.8 Hz, 1H), 7.31–7.26 (m, 3H), 2.54 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 197.4, 138.0, 136.8, 133.6, 132.5, 132.1, 130.1, 129.5, 129.4, 127.9, 127.0, 26.6.

*4.2.21. Ethyl 4-(phenylselanyl)benzoate (**1u**).*[7a] The reaction of 5 h, purification by column chromatography (petroleum ether), a colorless oil (93 mg, 76% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.87 (d, $J$=8.3 Hz, 2H), 7.56 (m, 2H), 7.35 (m, 5H), 4.34 (q, $J$=7.1 Hz, 2H), 1.36 (t, $J$=7.1 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 157.5, 143.6, 131.6, 129.9, 129.4, 128.5, 127.5, 124.8, 123.0, 120.7, 115.9, 111.3.

*4.2.22. 1-Naphthyl-phenyl-selenide (**1v**).*[15] The reaction of 5 h, purification by column chromatography (petroleum ether), a yellow liquid (79 mg, 70% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 8.37–8.31 (m, 1H), 7.85 (d, $J$=7.8 Hz, 2H), 7.77 (d, $J$=7.1 Hz, 1H), 7.55–7.47 (m, 2H), 7.40–7.31 (m, 3H), 7.20 (m, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 134.1, 133.86 (s), 131.7, 131.5, 129.3, 128.6, 127.7, 127.0, 126.8, 126.4, 126.0.

*4.2.23. 2-Methoxyphenyl-phenyl-selenide (**1w**).*[13] The reaction of 5 h, purification by column chromatography (petroleum ether), a colorless oil (60 mg, 55% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.58 (dd, $J$=7.5, 1.8 Hz, 2H), 7.33 (m, 3H), 7.18 (t, $J$=7.7 Hz, 1H), 6.95 (dd, $J$=7.7, 1.5 Hz, 1H), 6.85 (d, $J$=8.1 Hz, 1H), 6.78 (t, $J$=7.2 Hz, 1H), 3.88 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 156.6, 135.4, 130.8, 129.4, 128.3, 128.1, 127.7, 121.9, 121.6, 110.4, 55.9.

*4.2.24. 4-Fluoro-5-(phenylselanyl)pyridine (**1x**).* The reaction of 5 h, purification by column chromatography (petroleum ether/ethyl acetate=50:1), a pale yellow liquid (94 mg, 93% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 8.32 (m, 1H), 7.86 (ddd, $J$=8.4, 7.7, 2.4 Hz, 1H), 7.44 (m, 2H), 7.28 (m, 3H), 6.86 (dd, $J$=8.4, 2.9 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 164.0, 162.4, 151.5, 151.4, 146.2, 146.1, 132.8, 130.1, 129.6, 127.9, 124.6, 124.6, 110.7, 110.5. HRMS calcd for $C_{11}H_8FNSe$ ($M^+$): 252.9806; found: 252.9803.

*4.2.25. 2-Phenylselenyl-furan (**1y**).*[11b] The reaction of 5 h, purification by column chromatography (petroleum ether), a yellow oil (54 mg, 60% yield). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.59 (m, 1H), 7.34 (m, 2H), 7.27–7.19 (m, 3H), 6.76 (dd, $J$=3.2, 0.7 Hz, 1H), 6.45 (dd, $J$=3.2, 1.9 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 147.1, 138.2, 131.6, 130.3, 129.3, 126.90, 120.8, 111.9.

*4.2.26. 2-(Phenylselanyl)benzofuran (**1z**).* The reaction of 5 h, purification by column chromatography (petroleum ether), a light yellow solid (66 mg, 60% yield), mp: 39.6–40.6 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.55 (d, $J$=7.8 Hz, 1H), 7.47 (d, $J$=5.5 Hz, 3H), 7.30–7.20 (m, 7H), 7.03 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ 157.5, 143.6, 131.6, 129.9, 129.4, 128.5, 127.5, 124.8, 123.0, 120.7, 115.9, 111.3. HRMS calcd for $C_{14}H_{10}OSe$ ($M^+$): 273.9897; found: 273.9899.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.124. These data include MOL files and InChiKeys of the most important compounds described in this article.

## References and notes

1. (a) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125; (b) Hansen, D.; Peter, J. *Environ. Sci. Technol.* **1998**, *32*, 591; (c) Adeloju, S. B.; Bond, A. M. *Anal. Chem.* **1983**, *55*, 2076; (d) Szczepina, M. G.; Johnston, B. D.; Yuan, Y.; Svensson, B.; Pinto, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 12458.
2. (a) Perin, G.; Lenardão, E. J.; Jacob, R. G.; Panatieri, R. B. *Chem. Rev.* **2009**, *109*, 1277; (b) Mukherjee, A. J.; Zade, S. S.; Singh, H. B.; Sunoj, R. B. *Chem. Rev.* **2010**, *110*, 4357; (c) Freudendahl, D. M.; Shahzad, S. A.; Wirth, T. *Eur. J. Org. Chem.* **2009**, 1649; (d) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8409; (e) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400; (f) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205; (g) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596.
3. (a) Hellberg, J.; Remonen, T.; Johansson, M.; Inganäs, O.; Theander, M.; Engman, L.; Eriksson, P. *Synth. Met.* **1997**, *84*, 251; (b) Ando, T.; Kwon, T. S.; Kitagawa, A.; Tanemura, T.; Kondo, S.; Kunisada, H.; Yuki, Y. *Macromol. Chem. Phys.* **1996**, *197*, 2803.
4. (a) Testaferri, L.; Tiecco, M.; Tingoli, D.; Montanucci, M. *Synthesis* **1983**, 751; (b) Suzuki, H.; Abe, H.; Suka, A. *Chem. Lett.* **1981**, 151.
5. (a) Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667; (b) Rossi, R. A.; Peñéñory, A. B. *J. Org. Chem.* **1981**, *46*, 4580.
6. Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1458.
7. (a) Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *J. Organomet. Chem.* **2000**, *605*, 96; (b) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *Organometallics* **1985**, *4*, 657.
8. Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725.
9. Narayanaperumal, S.; Alberto, E. E.; de Andrade, F. M.; Lenardão, E. J.; Taube, P. S.; Braga, A. L. *Org. Biomol. Chem.* **2009**, *7*, 4647.

10. (a) Bieber, L. W.; de Sá, A. C. P. F.; Menezes, P. H.; Gonçalves, S. M. C. *Tetrahedron Lett.* **2001**, *42*, 4597; (b) Narayanaperumal, S.; Alberto, E. E.; Gul, K.; Kawasoko, C. Y.; Dornelles, L.; Rodrigues, O. E. D.; Braga, A. L. *Tetrahedron* **2011**, *67*, 4723.
11. (a) Reddy, V. P.; Kumar, A. V.; Rao, K. R. *J. Org. Chem.* **2010**, *75*, 8720; (b) Bhadra, S.; Saha, A.; Ranu, B. C. *J. Org. Chem.* **2010**, *75*, 4864; (c) Reddy, V. P.; Kumar, A. V.; Swapna, K.; Rao, K. R. *Org. Lett.* **2009**, *11*, 951; (d) Bieber, L. W.; da Silva, M. F.; Menezes, P. H. *Tetrahedron Lett.* **2004**, *45*, 2735; (e) Kumar, S.; Engman, L. *J. Org. Chem.* **2006**, *71*, 5400; (f) Taniguchi, N.; Onami, T. *J. Org. Chem.* **2004**, *69*, 915; (g) Gujadhur, R. K.; Venkataraman, D. *Tetrahedron Lett.* **2003**, *44*, 81; (h) Gonçalves, L. C.; Fiss, G. F.; Perin, G.; Alves, D.; Jacob, R. G.; Lenardão, E. J. *Tetrahedron Lett.* **2010**, *51*, 6772; (i) Cheng, J.-H.; Yi, C.-L.; Liu, T.-J.; Lee, C.-F. *Chem. Commun.* **2012**, 8440; (j) Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *Tetrahedron Lett.* **2003**, *44*, 7039.
12. Recent examples for Chan-Lam type reaction: (a) Taniguchi, N. *J. Org. Chem.* **2007**, *72*, 1241; (b) Zhang, L.-L.; Zhang, G.-Y.; Zhang, M.-L.; Cheng, J. *J. Org. Chem.* **2010**, *75*, 7472; (c) Singh, B. K.; Appukkuttan, P.; Claerhout, S.; Parmar, V. S.; der Eycken, E. V. *Org. Lett.* **2006**, *8*, 1863; (d) Li, J.-H.; Bénard, S.; Neuville, L.; Zhu, J.-P. *Org. Lett.* **2012**, *14*, 5980; (e) Raghuvanshi, D. S.; Gupta, A. K.; Singh, K. N. *Org. Lett.* **2012**, *14*, 4326; (f) Chan, D. G.; Winternheimer, D. J.; Merlic, C. A. *Org. Lett.* **2011**, *13*, 2778; (g) Xu, J.; Luo, D.-F.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Fu, Y.; Liu, L. *Chem. Commun.* **2011**, 4300; (h) Dai, J.-J.; Liu, J.-H.; Luo, D.-F.; Liu, L. *Chem. Commun.* **2011**, 677; (i) Prokopcová, H.; Kappe, C. O. *Angew. Chem., Int. Ed.* **2009**, *48*, 2276.
13. Wang, L.; Ren, K.; Wang, M. *Org. Biomol. Chem.* **2009**, *7*, 4858.
14. (a) Wang, L.; Ren, K.; Wang, M. *Adv. Synth. Catal.* **2009**, *351*, 1586; (b) Li, Y.-M.; Wang, H.-F.; Li, X.-Y.; Chen, T.; Zhao, D.-F. *Tetrahedron* **2010**, *66*, 8583.
15. Alves, D.; Santos, C. G.; Paixão, M. W.; Soares, L. C.; de Souza, D.; Rodrigues, O. E. D.; Braga, A. L. *Tetrahedron Lett.* **2009**, *50*, 6635.
16. Ricordi, V. G.; Freitas, C. S.; Perin, G.; Lenardão, E. J.; Jacob, R. G.; Savegnago, L.; Alves, D. *Green Chem.* **2012**, *14*, 1030.
17. Xu, H.-J.; Zhao, Y.-Q.; Feng, T.; Feng, Y.-S. *J. Org. Chem.* **2012**, *77*, 2878.
18. Rossi, R. A.; Pierini, A. B.; Santiago, A. N. In *Organic Reactions*; Paqucttc, L. A., Ed.; Wiley-VCH: Weinheim, Germany, 1999; Chapter 1, p 8.