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PAPER

Synthesis of diaryl selenides using electrophilic selenium species and nucleophilic boron reagents in ionic liquids†

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We described herein the use of imidazolium ionic liquids [bmim]PF_6 and [bmim]BF_4 in the selective, metal and catalyst-free synthesis of unsymmetrical diaryl selenides by electrophilic substitution in arylboron reagents with arylselenium halides (Cl and Br) at room temperature. This is a general substitution reaction and it was performed with arylboronic acids or potassium aryltrifluoroborates bearing electron-withdrawing or electron-donating groups, affording the corresponding diaryl selenides in good to excellent yields. The ionic liquid [bmim][PF_6] was easily recovered and utilized for further substitution reactions.

Introduction

The versatility and applicability of organoselenium compounds in organic chemistry is well described in a great number of reviews[1] and books.[2] Organoselenium compounds are attractive synthetic targets because of their selective reactions,[1,2] their use as ionic liquids[3] and in asymmetric catalysis,[1b,4] their fluorescent properties[5] and because of their interesting biological activities.[6] Many classes of organoselenium compounds have been prepared and widely studied, and among them aryl- and vinyl selenides are certainly the most applied compounds in organic synthesis.[1,2] Regarding the selenium species used as starting material, the large number of methods to prepare those compounds can be classified in two main categories: (a) those that use electrophilic organoselenium and (b) those using nucleophilic organoselenium species.[1,2]

Alternatively, transition metal-catalyzed reactions of diaryl diselenides with aryl halides or organoboron species has become a versatile tool for the synthesis of diaryl selenides.[7] Generally these transition metal-catalyzed reactions involve particularly specific ligands, which may increase the cost and limit the scope of applications. In recent years, electrophilic substitution by $ArSe^+$ in milder nucleophiles, such as boronic acids and esters, aryl siloxanes and aryl stannanes emerged as a good strategy to synthesize diorganyl selenides.[8] For example, Ranu and co-workers described the use of alumina-supported copper sulfate in the electrophilic substitution reactions of organoborane, organosilanes and organostannanes by phenylselenium bromide, providing a novel and efficient route to the synthesis of diaryl selenides.[8a]

In this sense, the development of environmentally benign and clean synthetic methods for the synthesis of diarylselenides, including those involving solvent-free or the use of alternative solvents, has increased in recent years. In this way, ionic liquids (ILs), especially those based on the 1,3-dialkylimidazolium cation, constitute an interesting alternative for organic reactions.[9] Because their negligible vapor pressure, nonflammability, reasonable thermal stability, ease of handling, potential for recycling product isolation or catalyst recycling and, in some cases, rate acceleration and/or selectivity improvements, they are regarded as environmentally friendly green solvents.[9] Ionic liquids were used as solvent in a range organic reactions,[10] such as palladium-catalyzed reactions,[10a] olefin metathesis[10b] and asymmetric synthesis,[10c] and have shown enhanced reaction rates when compared with conventional organic solvents.

Recently, the use of ILs in the synthesis of organochalcogen compounds has been described.[7d,8b,11] For example, vinylic selenides were obtained by the reaction of phenylselenyl chloride with vinylboronic acids or vinylboronic esters using [bmim][BF_4] as solvent and the products were isolated in good yields and stereospecifity.[8b] However, to the best of our knowledge, no reactions using aryl boronic acids or potassium aryltrifluoroborates as substrate in these reactions have been described so far.

Results and discussion

In this sense and due to our interest on green protocols correlated to the organochalcogen chemistry,[12] we describe here the use

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of imidazolium ionic liquids [bmim]BF_4 and [bmim]PF_6 in the synthesis of diaryl selenides by electrophilic substitution in arylboron reagents with arylselenium halides (Cl and Br) (Scheme 1).

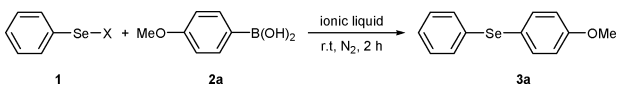
Scheme 1 General scheme of reaction.

We initially focused our attention on the optimization of the reaction conditions for the synthesis of 4-methoxyphenyl-phenyl selenide **3a** starting from electrophilic selenium species and nucleophilic boron reagents in imidazolium ionic liquids (Table 1). Firstly, phenylselenium chloride **1a** (0.3 mmol) was reacted with 4-methoxyphenylboronic acid **2a** (0.3 mmol) in [bmim][BF_4] (0.6 mL) at room temperature under nitrogen atmosphere. Under these conditions, the desired product **3a** was obtained in 86% (Table 1; entry 1). Aiming to improve the yield of reaction, a variety of electrophilic selenium species were tested, but no enhancement in yield was observed (Table 1; entry 1 *vs.* 2–4).

We observed that the nature of the ionic liquid was important for the reaction success (Table 1; entries 1, 5–7). Phenylselenium chloride **1a** and arylboronic acid **2a** was reacted with different imidazolium ionic liquids, such as, [bmim][BF_4], [bmmim][BF_4], [bmim][NTf_2] and [bmim][PF_6], and to our satisfaction, using [bmim][PF_6], the corresponding product **3a** was obtained in 95% yield after 2 h (Table 1; entry 7). A decrease in the yield of product **3a** was observed when the reaction was performed in open atmosphere (Table 1; entry 8). When the reaction was carried out using diphenyl diselenide instead of phenylselenium chloride **1a**, no product **3a** was obtained and the diphenyl diselenide was recovered quantitatively (Table 1; entry 9).

In an optimized reaction, phenylselenium chloride **1a** (0.3 mmol) was dissolved in [bmim][PF_6] (0.6 mL) and reacted with 4-methoxyphenylboronic acid **2a** (0.3 mmol) at room temperature under nitrogen atmosphere during 2 h, yielding 4-methoxyphenyl-phenylselenide **3a** in 95% yield (Table 1; entry 7). The formation of the product was easily observed by the change of the reaction color from dark orange to white (Fig. 1, a → c).

Table 1 Reaction conditions optimization using arylboronic acid **2a**[a]



1 2a 3a

Entry	X	Ionic liquid	Yield of **3a** (%)
1	Cl	[bmim][BF_4]	86
2	Br	[bmim][BF_4]	54
3	Suc	[bmim][BF_4]	42
4	Phthal	[bmim][BF_4][b]	84
5	Cl	[bmmim][BF_4]	73
6	Cl	[bmim][NTf_2]	70
7	Cl	[bmim][PF_6]	95
8	Cl	[bmim][PF_6][c]	82
9	SePh	[bmim][PF_6]	—

[a] Reactions performed in the presence of selenium electrophile (0.3 mmol), arylboronic acid **2a** (0.3 mmol) and ionic liquid (0.6 mL) at room temperature under nitrogen atmosphere. [b] 1.2 mL of [bmim][BF_4] was used. [c] Reaction was performed in open atmosphere.

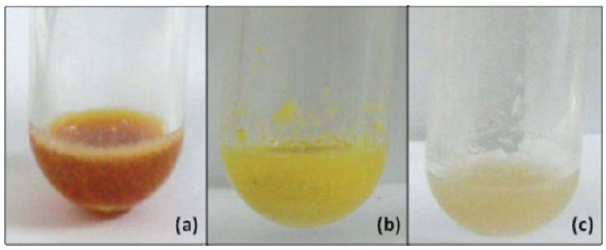


Fig. 1 Progress of the reaction between **1a** and **2a** in [bmim][PF_6]: (a): beginning of the reaction; (b): during the reaction (1 h); (c): at the end of the reaction (2 h).

In order to demonstrate the efficiency of this protocol, we explored the generality of our methodology by reacting other arylboronic acids **2b–k** with phenylselenium chloride **1a** (Table 2). The results disclosed in Table 2 reveal that the reaction worked well with a range of substituted arylboronic acids, affording excellent yields of the desired diarylselenides. In a general way, the reactions are little sensitive to the electronic effect of the aromatic ring in the arylboronic acid. For example, arylboronic acids containing electron-donating group (EDG) at the aromatic ring gave a slightly higher yield than those bearing electron-withdrawing group (EWG) and electron-neutral one (Table 2, entries 1–4 *vs.* 5–10).

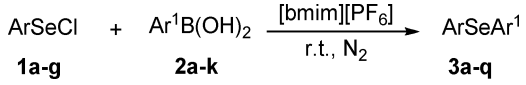
When the reaction was performed with 2-naphthylboronic acid **2k**, the respective product **3k** was obtained in high yield (Table 2; entry 11). In addition, the possibility of performing the reaction with other arylselenium chlorides[13] was also investigated. 4-Methoxyphenylboronic acid **2a** was efficiently reacted with a range of arylselenium chlorides containing EDG and EWG at the aromatic ring, affording the respective diarylselenides **3l–p** in high yields (Table 2; entries 12–15). 2-Pyridylselenium chloride[13b] **1g** was efficiently reacted with arylboronic acid **2a** giving the product **3q** in good yield (Table 2; entry 16).

These reactions were also performed under focused microwave irradiation. High levels of product formation were observed in these experiments, and the best result was achieved after irradiation at 50 °C for 15 min, giving the desired diaryl selenides in excellent yields (Table 2; entries 1, 3, 5–6, 10–11).

Furthermore, a study regarding the recovering and reusing of the ionic liquid was also performed. After the reaction of phenylselenium chloride **1a** with 4-methoxyphenylboronic acid **2a** in [bmim][PF_6] was complete, the product was extracted with diethyl ether. The inferior, ionic liquid phase was separated and dried under vacuum. The recovered [bmim][PF_6] was used directly in the next cycle, maintaining its good level of efficiency even after being reused four times (Fig. 2). Diarylselenide **3a** was obtained in 95%, 94%, 93%, 93%, and 92% yields after successive cycles.

Additionally, the possibility of the reaction of electrophilic selenium species with potassium aryltrifluoroborates in ionic liquid was investigated. Thus, under our optimized reaction conditions, phenylselenium chloride **1a** (0.3 mmol) was reacted with potassium 4-methoxyphenyltrifluoroborate **4a** (0.3 mmol)

Table 2 Scope and generality in the synthesis of diaryl selenides **3a–q** using arylselenium chlorides **1a–g** and arylboronic acids **2a–k**[a]



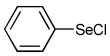
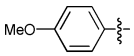
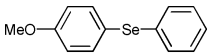
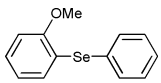
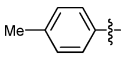
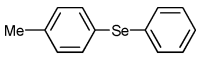
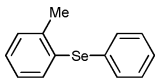
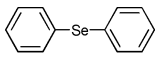
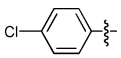
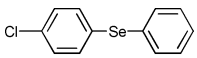
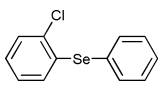
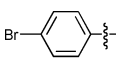
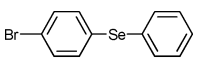
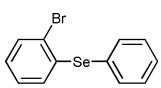
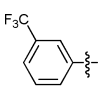
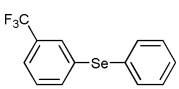
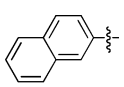
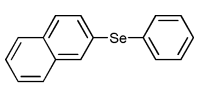
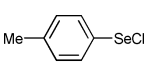
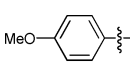
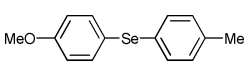
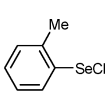
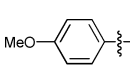
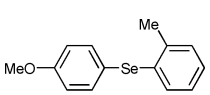
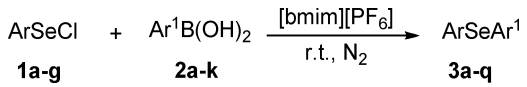
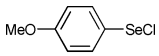
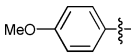
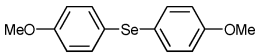
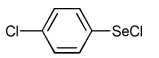
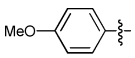
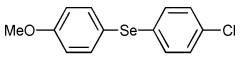
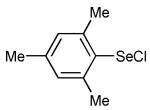
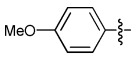
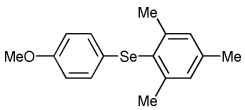
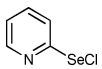
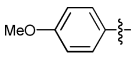
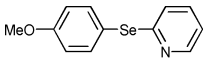
Entry	ArSeCl	Ar^1	Time (h)	Product	Yield (%)[b]
1	 **1a**	 **2a**	2	 **3a**	95 (95)
2	**1a**	 **2b**	3	 **3b**	94
3	**1a**	 **2c**	2	 **3c**	93 (94)
4	**1a**	 **2d**	4	 **3d**	92
5	**1a**	 **2e**	4	 **3e**	89 (91)
6	**1a**	 **2f**	6	 **3f**	86 (89)
7	**1a**	 **2g**	6	 **3g**	85
8	**1a**	 **2h**	6	 **3h**	92
9	**1a**	 **2i**	6	 **3i**	90
10	**1a**	 **2j**	4	 **3j**	75 (82)
11	**1a**	 **2k**	5	 **3k**	91 (91)
12	 **1b**	 **2a**	4	 **3l**	91
13	 **1c**	 **2a**	4	 **3m**	86

Table 2 (*Contd.*)



Entry	ArSeCl	Ar^1	Time (h)	Product	Yield (%)[b]
14	 **1d**	 **2a**	4	 **3n**	89
15	 **1e**	 **2a**	3	 **3o**	96
16	 **1f**	 **2a**	3	 **3p**	84
17	 **1g**	 **2a**	3	 **3q**	89

[a] Reactions performed in the presence of arylselenium chloride **1a–g** (0.3 mmol), arylboronic acid **2a–k** (0.3 mmol) in [bmim][PF_6] (0.6 mL) at room temperature under nitrogen atmosphere. [b] Yields in parenthesis correspond to reactions performed in a microwave reactor at 50 °C for 15 min.

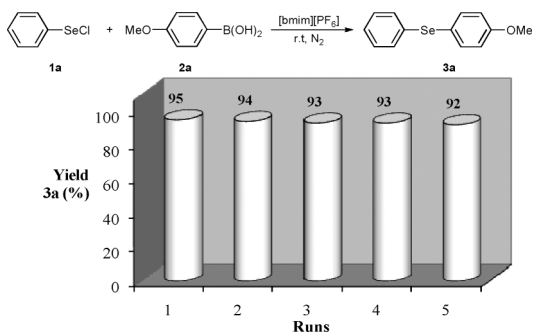
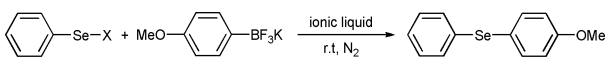


Fig. 2 Reuse of [bmim][PF_6] in the synthesis of **3a**.

Table 3 Reaction conditions optimization using aryltrifluoroborate **4a**[a]



Entry	X	Ionic liquid	Yield of **3a** (%)
1	Cl	[bmim][PF_6]	71
2	Br	[bmim][PF_6]	75
3	Suc	[bmim][PF_6]	69
4	Phthal	[bmim][PF_6][b]	73
5	Br	[bmim][BF_4]	88
6	Br	[bmmim][BF_4]	65
7	Br	[bmim][NTf_2]	54
8	Br	[bmim][BF_4][c]	79

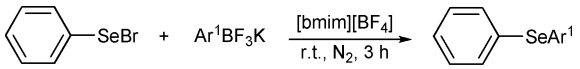
[a] Reactions performed in the presence of selenium electrophile (0.3 mmol), potassium aryltrifluoroborate **4a** (0.3 mmol) and ionic liquid (0.6 mL) at room temperature under nitrogen atmosphere. [b] 1.2 mL of [bmim][PF_6] was used. [c] Reaction was performed in open atmosphere.

in [bmim][PF_6] (0.6 mL) at room temperature and the product **3a** was obtained in 71% isolated product yield (Table 3, entry 1). In view of this satisfactory result, different electrophilic selenium species and ionic liquids were tested aiming to increase the yield of product **3a** (Table 3).

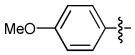
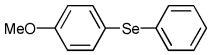
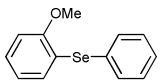
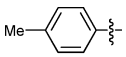
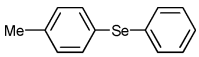
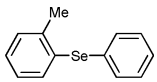
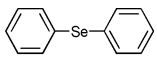
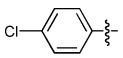
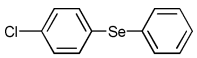
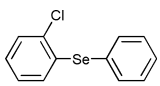
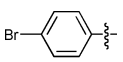
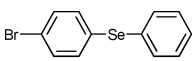
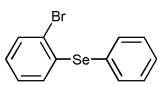
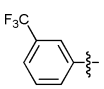
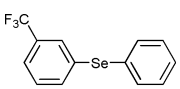
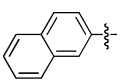
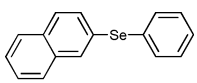
When the reaction was performed using phenylselenium bromide **1i**, an increase in the product yield was observed (Table 3; entry 2). To our satisfaction, using phenylselenium bromide **1i** (0.3 mmol), potassium 4-methoxyphenyltrifluoroborate **4a** and [bmim][BF_4] (0.6 mL) instead [bmim][PF_6], the reaction proceeds smoothly and 4-methoxyphenyl-phenylselenide **3a** was obtained in 88% yield after stirring for 3 h (Table 3; entry 5). Using other ionic liquids, such as, [bmmim][BF_4] and [bmim][NTf_2], a decrease in the yields are observed (Table 3; entries 6–7). When the reaction of phenylselenium bromide **1i** with potassium aryltrifluoroborate **4a** in [bmim][BF_4] was carried out in open atmosphere, product **3a** was formed in reduced yield (Table 3; entry 8).

The scope of the reaction regarding the use of different potassium aryltrifluoroborates was examined and excellent results were obtained (Table 4). Diaryl selenides containing both electron-donating (entries 1–4) and electron-withdrawing groups (entries 6–10), were obtained in comparable yields, except **3j** (EWG = CF_3) which was obtained in 73% yield (entry 10). Potassium naphthyltrifluoroborate **4k** reacts efficiently with phenylselenium bromide **1i** furnishing product **3k** in good yield (Table 4; entry 11).

Table 4 Synthesis of diaryl selenides **3a–k** using phenylselenium bromide **1i** and aryltrifluoroborates **4a–k**[a]



1h **4a-k** **3a-k**

Entry	Ar^1	Product	Yield (%)
1	 **4a**	 **3a**	88
2	 **4b**	 **3b**	85
3	 **4c**	 **3c**	86
4	 **4d**	 **3d**	86
5	 **4e**	 **3e**	85
6	 **4f**	 **3f**	84
7	 **4g**	 **3g**	81
8	 **4h**	 **3h**	86
9	 **4i**	 **3i**	82
10	 **4j**	 **3j**	73
11	 **4k**	 **3k**	84

[a] Reactions performed in the presence of phenylselenium bromide **1i** (0.3 mmol), potassium aryltrifluoroborate **4a–k** (0.3 mmol) in [bmim][BF_4] (0.6 mL) at room temperature under nitrogen atmosphere for 3 h.

Conclusions

In conclusion, imidazolium ionic liquids [bmim]BF_4 and [bmim]PF_6 are very efficient to promote the selective synthesis of unsymmetrical diaryl selenides in high yields under mild conditions. By changing the anion in the ILs is possible achieve very good results using both, arylboronic acids or potassium aryltrifluoroborates as starting nucleophiles. Another benefit of the described procedure is not being necessary the use neither of metal nor catalyst, another green facet of this new protocol is the recyclability of the solvent without any pre-treatment.

Experimental

General

The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. NMR spectra were recorded with Bruker DPX 200 and DPX 400 (200 and 400 MHz) instrument using $CDCl_3$ as solvent and calibrated using tetramethylsilane as internal standard. Chemical shifts are reported in δ (ppm) relative to $(CH_3)_4Si$ for ^1H and $CDCl_3$ for ^{13}C NMR. Coupling constants (J) are reported in Hertz. Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 mass spectrometer. Microwave reactions were conducted using a CEM Discover, mode operating systems working at 2.45 GHz, with a power programmable from 1 to 300 W.

General procedure for the reaction of electrophilic selenium species with nucleophilic boron reagents

In a Schlenk tube under nitrogen atmosphere containing ionic liquid ([bmim][PF_6] or [bmim][BF_4]) (0.6 mL) and nucleophilic boron reagent [$ArB(OH)_2$ or $ArBF_3K$] (0.3 mmol), the corresponding arylselenium halide (ArSeCl or ArSeBr) (0.3 mmol) was added in one portion. The reaction mixture was allowed to stir at room temperature for the time indicated in Table 2 and 4. After the reaction was complete, the products were extracted into diethyl ether (3 × 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate/hexanes as the eluent.

4-Methoxyphenyl-phenyl-selenide (3a)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, J = 8.8 Hz, 2H); 7.33–7.31 (m, 2H); 7.21–7.16 (m, 3H); 6.84 (d, J = 8.4 Hz, 2H); 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.7, 136.5, 133.2, 130.9, 129.1, 126.4, 119.9, 115.1, 55.2. MS (relative intensity) m/z: 264 (65), 262 (34), 184 (100), 153 (32), 65 (14).

2-Methoxyphenyl-phenyl-selenide (3b)[14]. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.61–7.56 (m, 2 H), 7.35–7.31 (m, 3 H), 7.24–7.14 (m, 1 H), 6.97–7.74 (m, 3 H), 3.88 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$); δ (ppm): 156.9, 135.2, 131.2, 129.4, 128.6, 127.9, 127.8, 122.0, 121.6, 110.6, 55.9. MS (relative intensity) m/z: 264 (65), 262 (33), 184 (100), 169 (40), 141 (33), 77 (32).

4-Tolyl-phenyl-selenide (3c)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.32 (m, 4H); 7.23–7.16 (m, 3H); 7.04 (d, J = 8.5 Hz, 2H); 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 137.6, 133.8, 132.0, 130.1, 129.1, 126.8, 21.1. MS (relative intensity) m/z: 248 (70), 246 (39), 168 (100), 153 (25), 91 (63), 65 (30).

2-Tolyl-phenyl-selenide (3d)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.38 (m, 2H); 7.35–7.32 (m, 1H); 7.27–7.17 (m, 5H); 7.08–7.04 (m, 1H); 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 139.8, 133.6, 132.7, 131.7, 130.7, 130.2, 129.3, 127.7, 127.1, 126.7, 22.3. MS (relative intensity) m/z: 248 (72), 246 (37), 168 (100), 153 (20), 91 (57), 65 (32).

Diphenyl-selenide (3e)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.46–7.44 (m, 4H); 7.24–7.21 (m, 6H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 132.9, 131.1, 129.3, 127.2. MS (relative intensity) m/z: 234 (30), 154 (100), 77 (20), 51 (17).

4-Chlorophenyl-phenyl-selenide (3f)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.46–7.44 (m, 2H); 7.36 (d, J = 8.0 Hz, 2H); 7.28–7.26 (m, 3H); 7.21 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 134.1, 133.5, 133.1, 130.6, 129.5, 129.4, 127.6. MS (relative intensity) m/z: 270 (15), 268 (36), 188 (100), 152 (27), 77 (22), 51 (18).

2-Chlorophenyl-phenyl-selenide (3g)[14]. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.65–7.58 (m, 2H); 7.41–7.23 (m, 4H); 7.15–6.98 (m, 2H), 6.91 (dd, J = 7.6, 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 135.9, 133.9, 131.6, 131.0, 129.7, 129.4, 128.7, 128.2, 127.4, 127.3. MS (relative intensity) m/z: 270 (19), 268 (41), 188 (100), 152 (32), 77 (19), 51 (19).

4-Bromophenyl-phenyl-selenide (3h)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.46–7.44 (m, 2H); 7.34 (d, J = 8.4 Hz, 2H); 7.28–7.25 (m, 5H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 134.1, 133.2, 133.0, 130.4, 130.3, 129.4, 127.6, 121.41. MS (relative intensity) m/z: 314 (68), 312 (86), 234 (84), 232 (99), 152 (100), 116 (27), 77 (58), 51 (41).

2-Bromophenyl-phenyl-selenide (3i)[15]. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.66–7.62 (m, 2 H), 7.52–7.38 (m, 4 H), 7.07–7.00 (m, 2 H), 6.88–6.83 (m, 1 H). ^{13}C NMR ($CDCl_3$ 50 MHz); δ (ppm): 136.4, 136.2, 132.7, 130.4, 129.8, 128.9, 128.4, 127.8, 127.3, 123.4. MS (relative intensity) m/z: 312 (61), 232 (58), 207 (27), 156 (22), 152 (100), 77 (50).

3-(Trifluoromethyl)phenyl-phenyl-selenide (3j)[16]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.67 (s, 1H); 7.53–7.44 (m, 4H); 7.31–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 135.1, 134.0, 133.2, 131.5 (q, J = 32.2 Hz), 129.6, 129.5, 129.4, 128.4 (q, J = 3.8 Hz), 128.2, 123.7 (q, J = 272.8 Hz), 123.6 (q, J = 3.8 Hz). MS (relative intensity) m/z: 302 (55), 222 (100), 153 (16), 77 (35), 51 (24).

2-Naphthyl-phenyl-selenide (3k)[17]. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.98–7.97 (m, 1 H), 7.80–7.69 (m, 3 H), 7.53–7.43 (m, 5 H), 7.27–7.24 (m, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$); δ (ppm): 133.9, 132.8, 132.3, 132.0, 131.2, 130.4, 129.3, 128.7, 128.4, 127.7, 127.4, 127.3, 126.5, 126.2. MS (relative intensity) m/z: 284 (24), 204 (100), 126 (11), 115 (19), 77 (11).

4-Tolyl-4-methoxylphenyl-selenide (3l)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.8 Hz, 2H); 7.26 (d, J = 8.0 Hz, 2H); 7.00 (d, J = 8.0 Hz, 2H); 6.79 (d, J = 8.8 Hz, 2H); 3.72 (s, 3H); 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.4, 136.5, 135.6, 131.7, 129.9, 128.8, 120.8, 114.9, 55.1, 20.9. MS (relative intensity) m/z: 278 (65), 198 (100), 183 (43), 170 (33), 91 (32), 65 (22).

2-Tolyl-4-methoxylphenyl-selenide (3m)[14]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 8.8 Hz, 2H), 7.14–7.06 (m, 3H), 6.99–6.95 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.7, 137.8, 136.5, 133.8, 130.7, 129.9, 126.5, 119.2, 115.2, 55.2, 21.8. MS (relative intensity) m/z: 278 (71), 198 (100), 183 (37), 170 (30), 91 (26), 65 (24).

Bis-4-methoxylphenyl-selenide (3n)[18]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, J = 8.9 Hz, 4H), 6.65 (d, J = 8.9 Hz, 2H), 3.59 (s, 6H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.1,

134.4, 121.9, 114.8, 55.1. MS (relative intensity) *m/z*: 294 (71), 214 (100), 186 (42), 65 (17).

4-Chlorophenyl-4-methoxylphenyl-selenide (3o)[14]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.8 Hz, 2H); 7.21 (d, J = 8.8 Hz, 2H); 7.14 (d, J = 8.8 Hz, 2H); 6.83 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 159.9, 136.6, 132.4, 132.0, 131.5, 129.1, 119.4, 115.2, 55.2. MS (relative intensity) *m/z*: 298 (35), 296 (17), 218 (100), 203 (40), 175 (27), 63 (12).

1,2,3-(trimethyl)phenyl-4-methoxylphenyl-selenide (3p). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.95 (d, J = 8.8 Hz, 2H), 6.83 (s, 2H), 6.59 (d, J = 8.8 Hz, 2H), 3.58 (s, 3H), 2.33 (s, 6H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz); δ (ppm): 158.0, 143.2, 138.6, 130.6, 128.7, 127.8, 123.1, 114.8, 55.1, 24.2, 20.9. MS (relative intensity) *m/z*: 306 (100), 226 (54), 211 (22), 197 (78), 183 (18), 119 (25), 105 (12), 91 (40), 77 (25), 63 (8). HRMS calcd for $C_{16}H_{18}OSe$: 306.0523. Found: 306.0528.

2-Pyridyl-4-methoxylphenyl-selenide (3q). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.41 (ddd, J = 4.9, 1.9, 0.8 Hz, 1H); 7.63 (d, J = 8.9 Hz, 2H); 7.36 (ddd, J = 7.5, 4.9, 1.9 Hz, 1H); 7.01–6.88 (m, 4H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$ 50 MHz); δ (ppm): 160.3, 159.8, 149.6, 138.2, 136.5, 123.3, 120.0, 117.6, 115.3, 55.2. MS (relative intensity) *m/z*: 265 (68), 264 (100), 262 (63), 249 (21), 185 (25), 142 (15), 78 (59), 51 (32). HRMS calcd for $C_{12}H_{11}NOSe$: 265.0006. Found: 265.0011.

General procedure to microwave reactions of phenylselenium chloride 1a with arylboronic acids in [bmim][PF$_6$]

In a 10 mL glass vial, under nitrogen atmosphere, equipped with a small magnetic stirring bar, containing the appropriate arylboronic acid (0.3 mmol) and [bmim][PF_6] (0.6 mL) was added PhSeCl **1a** (0.3 mmol). The mixture was then irradiated in a focused microwaves reactor (CEM Explorer) at 50 °C, using an irradiation power of 50 W. After stirring for 10 min, the products were extracted into diethyl ether (3× 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate/hexanes as the eluent.

Recycle of [bmim][PF$_6$] in the reaction of phenylselenium chloride 1a with arylboronic acid 2a

In a Schlenk tube under nitrogen atmosphere containing ionic liquid [bmim][PF_6] (0.6 mL) and 4-methoxyphenylboronic acid **2a** (0.3 mmol), phenylselenium chloride **1a** (0.3 mmol) was added in one portion. The reaction mixture was allowed to stir at room temperature for 2 h. After the reaction was complete, the products were extracted into diethyl ether (3× 5 mL), dried over $MgSO_4$, and concentrated under vacuum. The inferior, ionic liquid phase, was separated and dried under vacuum. The recovered [bmim][PF_6] was used directly in the next cycle.

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