

Metal-free and Atom-efficient Protocol for Diarylation of Selenocyanate by Diaryliodonium Salts

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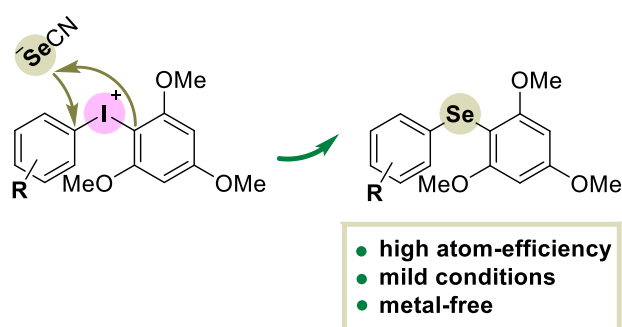
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Abstract. The rational search for the efficient protocols for atom-efficient arylation utilizing iodonium salts is the genuine need for the sustainability and green chemistry. We developed a novel approach toward metal-free diarylation of selenocyanate using trimethoxyphenyl-substituted iodonium salts with the formation of appropriate diarylselenides. The suggested procedure allows the preparation of a series of diarylselenides without isolation and purification of intermediate products in two-step one-pot sequence.

Graphical Abstract



Keywords: diaryliodonium salts, diarylation, atom-efficiency, selenocyanate, metal-free substitution

Introduction

Diaryliodonium salts (IS) are among the most widely used types of hypervalent iodine reagents.¹⁻⁷ These iodine(III) derivatives, in particular, found their bright place in the palette of arylation reagents thank to exceptional leaving group properties of iodoarenes.⁸ This property makes IS a close-to-perfect source of electrophilic aromatic carbon for the arylation of various nucleophiles, including halogenides, pseudohalogenides, and varieties of C-, O-, N-centered organic nucleophiles.^{3,9,10}

Despite the progress in the arylations involving IS,^{6,11-13} these methods exhibit a considerable disadvantage associated with the generation of iodoarene formed along with the target compound (**Figure 1-Common strategy**). In view of that, the atom-efficiency (AE) of the arylations which utilize IS is far from the requirements of modern organic syntheses in terms of sustainability and green approaches. An attractive route to increase AE is *diarylation* of nucleophilic centers using IS as a source of *both* aryl groups.^{14,15} However, the reactivity of iodoarenes, generated after the first arylation step, is rather low and its enhancement requires transition metal catalysts.^{16,17}

The nucleophilic substitution on chalcogen-center is promising reaction for the design and preparation of the wide range of valuable compounds.¹⁸⁻²¹ Indeed, the exceptional properties of IS as arylation agents led to the development of useful synthetic methods for the chemistry of arylchalcogenides.²²⁻²⁴ However, the *diarylation* procedures, which include the involvement of both aryl moieties, are still poorly developed.^{12,13}

To date, the *diarylation* of chalcogen-containing species by IS was conducted mainly under Cu- or Fe-based catalytic conditions.²⁵⁻²⁸ These approaches for metal-catalyzed *diarylations* are characterized by a relatively low AE and complex sources of the nucleophilic chalcogen. The metal-free *diarylations* of chalcogen-centered nucleophiles, until the year 2022, has been successfully realized only in cases of cyclic iodonium salts.^{29,30} The maximum AE in these reactions has been achieved by Jiang et al.²⁹ for S₈ or Se, acting as chalcogen sources,

namely 28–40% for the prepared sulfides and 48–58% for selenides. These reactions—with the involvement of *both* aryl groups and the release of the iodine atom from the target molecule—improved the AE from poor to good (**Figure 1-Diarylation strategy**). Very recently, Olofsson and coworkers pioneered in the transition metal-free strategy to AE diarylation of various nucleophiles,¹⁴ in particular, toward the preparation of diarylsulfides³¹ from unsymmetric diaryliodonium salts. Very high AE (up to 83%) was reached by the retention of the I atom in the products (**Figure 1-Olofsson strategy**).

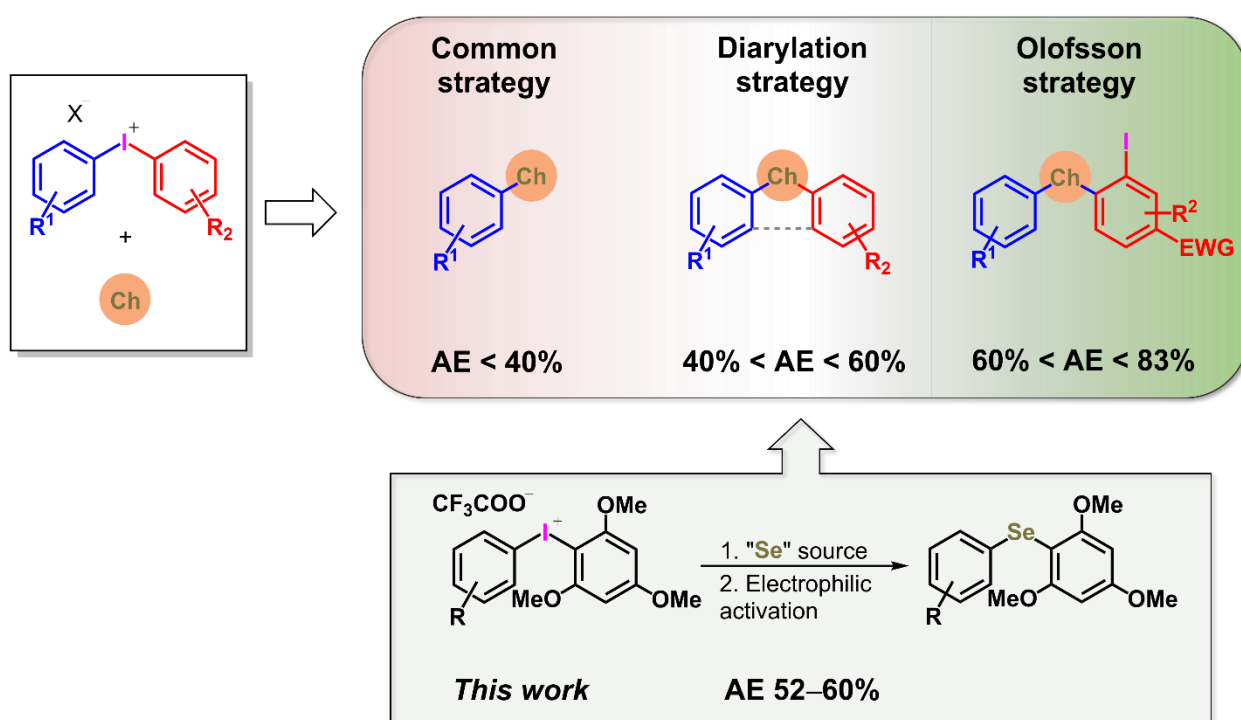


Figure 1. Diarylation of chalcogenides by IS.

The arylation of Se-based nucleophiles plays a special role in the preparation of valuable diarylselenides.^{15,29} Townsend et al.¹⁵ reported the generation of ArSeCN from IS and KSeCN, as a source of the nucleophilic [Se⁻], followed by the reduction and additional arylation of the formed selenol, ArSeH, by one more equivalent of IS. This approach also accomplished significant amounts of aryl iodides, formed as by-products, and expectedly this method is characterized by rather poor AE (25–28%).

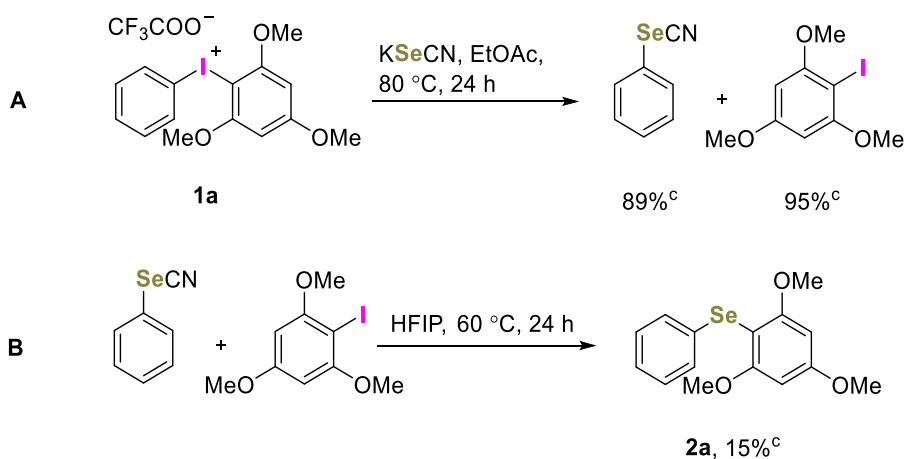
The chemistry of ArSeCN, however, provides an exciting option which helps to increase AE. Withal, Goswami and coworkers³² reported the arylation of ArSeCN by electron-rich arenes via electrophilic activation of the SeCN moiety by hydrogen bond donating hexafluoroisopropanol (HFIP). We assumed that their approach, including the choice of reactants and the solvent, can be extended to unsymmetrical diaryliodonium salts bearing an electron-rich auxiliary group. Application of unsymmetric IS in the arylations is primarily associated with the employment of electron-rich arenes (2,4,6-trimethoxyphenyl (abbreviated as TMP),^{18,33-40} thienyl,⁴¹⁻⁴³ etc.^{5,44}) – all functioning as leaving groups.

All these considerations allowed us to hypothesize that diarylselenides can be obtained using, on the one hand, diaryliodonium salts as a source of two aryl moieties and, on the other hand, the nucleophilic Se atom in SeCN⁻. Following this assumption, we developed a convenient and facile green method toward the preparation of TMP-substituted diarylselenides from diaryliodonium salts. The suggested approach includes two-step arylation of SeCN⁻ followed by an interplay with TMP-I (TMP-I is 2-iodo-1,3,5-trimethoxybenzene); the latter proceeds without isolation of the intermediate product and give good-to-high yields of the target TMP-substituted diarylselenides. All our results are consistently detailed in sections that follow.

Results and Discussion

We started experiments focused on the diarylation of SeCN⁻ with an extension of the earlier reported procedure¹⁵ to the TMP-substituted IS (**1**). Thus, ArSeCN was generated via a facile nucleophilic substitution reaction: the conventional heating of **1a** with KSeCN in EtOAc leads to PhSeCN in close-to-quantitative yield and with an exceptional selectivity (**Figure 2-A**). The observed selectivity is in a good agreement with that previously reported for the arylation using TMP-substituted IS.^{18,33-40} The arylation of SeCN⁻ by **1** should lead to equimolecular amounts of 2,4,6-trimethoxyphenyliodide and its occurrence decreases AE of the overall process (**Figure 2-A**). Considering the conventional reactivity mode of arylselenocyanates, namely their

ability to generate the electrophilic ArSe^+ species,⁴⁵⁻⁴⁷ we assumed that the reaction between *in situ* generated PhSeCN (an ArSe^+ synthon) with TMP-I (a TMP^- synthon) could accomplish the diarylated selenides. These transformations have been previously observed on the arylation of electron-rich arenes.³²



Footnote: ^a Reaction conditions: phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1a** (5 mmol), KSeCN (5.5 mmol), EtOAc (20 mL); ^b phenylselenocyanate (1 mmol), TMP-I (1.1 equiv.), HFIP (2 mL), inert conditions; ^c Isolated yield.

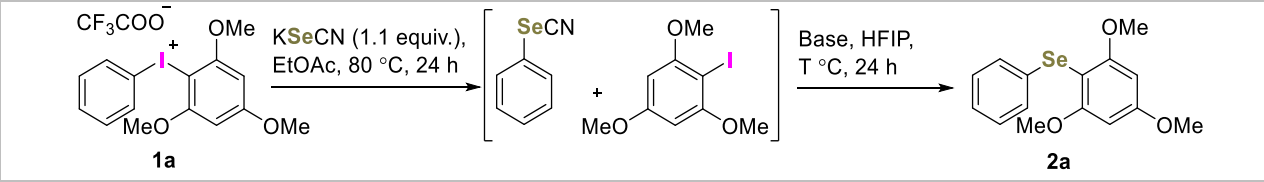
Figure 2. Arylation of SeCN^- by **1a** (A)^a and reaction of PhSeCN with TMP-I (B)^b.

Initially, for the diarylation we employed the previously reported conditions³² which include PhSeCN and TMP-I as the reactants and HFIP as a solvent. However, under these conditions the yield of the target product was only 15% (**Figure 2-B**; for details see the Supporting Information, **Table S1**) and therefore we focused on optimization of the diarylation and conductance of this reaction without isolation of intermediate products. In this way, we attempted to avoid an additional purification of intermediate products. Hence, we provided the arylation of SeCN^- using **1** and KSeCN ; the latter acts as the nucleophilic component of the arylation.

The first stage of the diarylation to give PhSeCN, was conducted in EtOAc, which was evaporated after the reaction completion. The second stage was performed on heating PhSeCN and TMP-I (without isolation) in HFIP. Such procedure accomplishes phenyl(2,4,6-trimethoxyphenyl)selane (**2a**), which was isolated in 15% yield (Entry 1; **Table 1**). The results of the reaction, which proceeds without isolation of intermediate products, reproduces well our experiments when we used the pure PhSeCN and TMP-I; this method also gave **2a** in 15% yield (**Figure 2-B**).

We assumed that yield of reaction can be improved by addition of a base capable of trapping the generated I⁺ species. Indeed, the addition of Et₃N gave almost 2-fold improved yield (28%). Further variation of bases indicates that the utilization of DIPEA leads to a poorer yield (23%, Entry 3; **Table 1**), while the employment of DMAP or KOH provides better yields (57% and 53%, respectively; Entries 4–5). At this stage of the optimization, the employment of pyridine, among the other tested bases, led the best results and **2a** was isolated in 65% yield (Entry 6; **Table 1**).

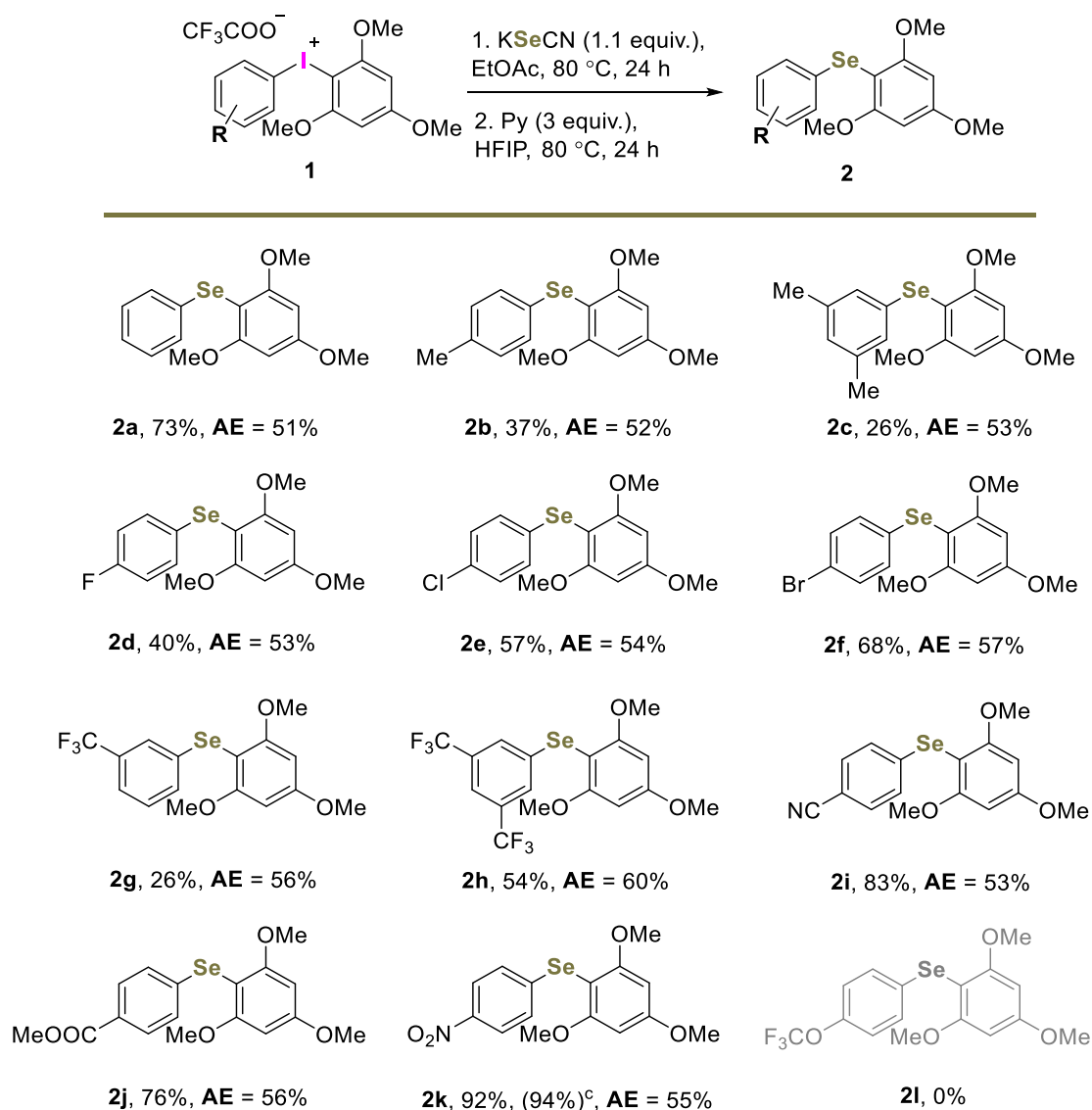
An increase in the reaction temperature gave 73% of **2a** (at 80 °C) vs. 65% (at 60 °C) (Entry 7; **Table 1**). To improve further the yield of **2a**, we continued the experiments verifying the role of bases (see above in this section). Surprisingly, 2-fold increased amount of pyridine (up to 6 equiv.) provided the same yield (73%, Entry 8; **Table 1**). The utilization of a pyridine:HFIP mixture as a reaction media completely suppressed the generation of the target product (0%, Entry 9; **Table 1**). We also checked an effect of the addition of HFIP to the reaction mixture in EtOAc after the generation of PhSeCN, but this experiment was unsuccessful and **2a** was found in only trace amounts (Entry 10; **Table 1**). Thus, the best conditions for the diarylation of **1** are as the following: the reaction should be performed at 80 °C for 24 h followed by replacement of the solvent (EtOAc to HFIP) and then again heating at 80 °C for 24 h in the presence of pyridine (3 equiv.).

Table 1. Optimization of the SeCN⁻ diarylation^a

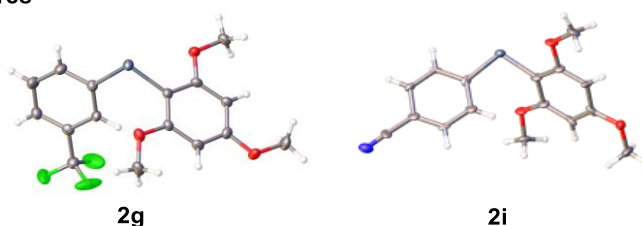
Entry ^a	Solvent	Base (equiv.)	Temperature, °C	Yield, % ^b
1	HFIP	–	60	15
2	HFIP	Et ₃ N (3)	60	28
3	HFIP	DIPEA (3)	60	23
4	HFIP	DMAP (3)	60	57
5	HFIP	KOH (3)	60	53
6	HFIP	Py (3)	60	65
7	HFIP	Py (3)	80	73
8	HFIP	Py (6)	80	73
9	HFIP/Py (1/1)		80	n.r.
10	EtOAc/HFIP (1/1)	Py (3)	80	trace

Footnote: ^a Reaction conditions: **1a** (0.25 mmol), KSeCN (0.275 mmol), EtOAc (2 mL), HFIP (2 mL); ^b Isolated yield.

To explore the substrate scope, various iodonium salts **1** were introduced in the reaction under the optimized conditions (**Figure 3**). The composition of reaction mixtures was monitored after the first stage of the arylation to prove the full conversion of the starting IS and then generation of the target ArSeCN. The reaction of **1**, bearing electron-donating methyl- and 3,5-dimethyl groups, gave only 23–28% yields of **2b,c** but satisfactory selectivity in the formation of ArSeCN. The reaction with (4-CF₃OC₆H₄)SeCN, generated from **1l**, did not proceed and the target product was not detected. On the contrary, ArSeCN, featuring such electron-withdrawing group as 4-CN, 4-COOMe, or 4-NO₂, efficiently reacted with TMP-I to give high yield (up to 92%) of the desired products **2i–k**. In the range of ArSeCN, bearing EWG aryls, only (3-CF₃C₆H₄)SeCN (**1g**) was converted to the target product although in a rather low (26%) yield. Incorporation of one more CF₃ group in the aryl moiety (**1h**) led to an increased yield of **2h** (54%). In the cases of 4-halo substituted salts **1d–f**, the yield of **2d–f** decreased in a series Br (68%) > Cl (57%) > F (26%) in agreement with appropriate electronic effects of these substituents.⁴⁸



X-ray structures



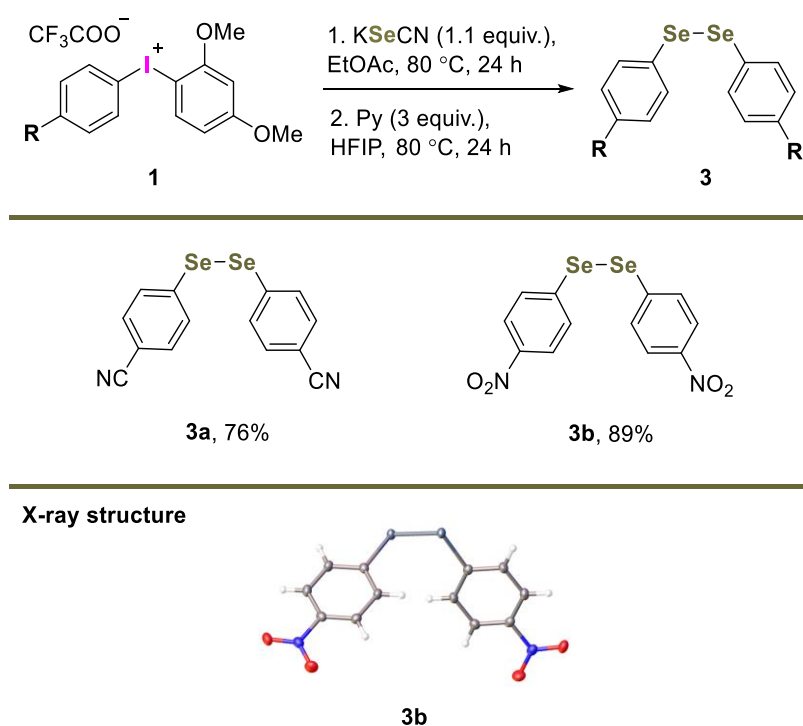
Footnote: ^a Reaction conditions: **1** (1 equiv. 0,25 mmol), KSeCN (1.1 equiv.), pyridine (3 equiv.), 24 h, 80 °C. ^b Isolated yield, ^c Gram-scale synthesis of **2k**: **1k** (3.5 mmol, 1.86 g).

Figure 3. Preparation of aryl(2,4,6-trimethoxyphenyl)selanes **2**.^{a,b}

The developed procedure was successfully scaled up. As an illustrative example, the reaction of **1k** in 3.5 mmol scale gave selenide **2k** in 94% yield (1.21 g); this yield is almost identical to that achieved for the reaction conducted in 0.25 mmol scale (92%, 85 mg).

AE is conventionally determined as the ratio of the molecular weight of the main product to the sum of the molecular weights of all reaction products.^{49,50} The implementation of the developed method for the preparation of diarylselenides gave significant AE (up to 60%) which is one of the highest among the other yields achieved in other strategies focused on the arylation of chalcogenides by diaryliodonium salts.⁵¹ To date, a higher AE has been only achieved by Olofsson and coworkers³¹ due to retention of iodine atom in the final structure.

We also attempted to verify an effect of electron-rich moieties on the arylation and prepared iodonium salts **1m,n** featuring 1,3-dimethoxybenzene (as an axially group). For all these compounds the arylation of SeCN^- proceeded smoothly and gave appropriate selenocyanides with high selectivity. However, the reaction of ArSeCN with 1-iodo-2,6-dimethoxybenzene led to only symmetrical diselenides **3a,b** (in high yields) instead of diarylselanes **2** (Figure 4).



Footnote: ^aReaction conditions: **1** (1 equiv. 0,25 mmol), KSeCN (1.1 equiv.), pyridine (3 equiv.), 24 h, 80 °C.

Figure 4. Synthesis of symmetric diselenides **3**.^a

Considering the observed reactivity of TMP-substituted IS, we postulated a plausible mechanism of the diarylation. We assumed that HFIP (functioning as an efficient hydrogen bond donor) activates ArSeCN species.⁵² Next step is the generation of a complex occurred between π -electrons of TMP-I and selenocyanate (**Figure 5**). The formation of the postulated π -complex should be facilitated by the presence of EDG-substituents in the iodoarene ring. In the case of 2,4-dimethoxyiodobenzene, where electron density is not sufficient for the generation of π -complex, the selenocyanates are able to interact with each other under basic conditions, as reported earlier.^{53,54} Notably, we did not approve a mechanism involving single-electron transfer⁵⁵⁻⁵⁸ as follows from our control experiments, which include the addition of TEMPO (for details see the Supporting Information, **Figure S2**).

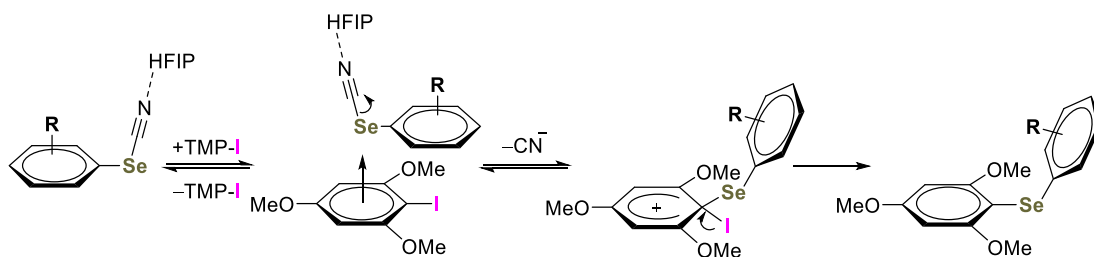


Figure 5. Plausible mechanism of the diarylation.

Conclusion

We developed procedure, which accomplishes diarylselenides bearing electron-donating TMP moieties after two-step reaction and the overall process was conducted without isolation of intermediate products. The diarylation is characterized by high atom-efficiency and does not require utilization of transition metal-based catalysts. We hope that our findings should stimulate the development of relevant atom-efficient synthetic methods for various diarylations using iodonium salts for the sustainable chemistry.

Acknowledgements

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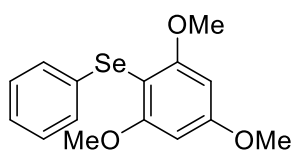
Experimental section

General information. All reagents and solvents were obtained from commercial sources and used without further purification. Iodonium salts were obtained by the previously reported procedures.⁵⁹ Thin layer chromatography (TLC) was performed using precoated plates purchased from Macherey–Nagel (silica gel 60, 0.20 mm). Column chromatography was performed on 63–200 μm silica gel purchased from Macherey–Nagel. Melting points were measured on a BUCHI M-560 apparatus in capillaries and are not corrected. NMR spectra were recorded on Bruker Avance III HD (400 MHz). ^1H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz, and ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts are reported in parts per million (ppm). ^1H and ^{13}C chemical shifts are referenced relative to the residual solvent signal. High-resolution mass spectra (HRMS) were recorded using atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) methods for **2c–e, g–k** on a Shimadzu LCMS-9030 Q-TOF mass spectrometer coupled with LC-30 UHPLC system.

X-ray structure determinations. X-ray diffraction data were collected at 100 K on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer using Cu $K\alpha$

($\lambda = 1.54184 \text{ \AA}$; **2g,i** and **3b**). The structures were solved with the ShelXT⁶⁰ structure solution program using Intrinsic Phasing and refined with the ShelXL⁶¹ refinement package incorporated in the OLEX2 program package⁶² using Least Squares minimization. XRD data and structural refinement parameters are summarized in **Table S2**. Hydrogen atoms in all structures are placed in ideal calculated positions accordingly to neutron diffraction statistical data⁶³ and refined as colliding atoms with parameters of relative isotropic displacement. Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC structures 2250168, 2250169, 2250170) and can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

General procedure for synthesis of diarylselenides 2a–k, 3a,b (GP1). Screw cap tube was charged with a mixture of iodonium salt **1** (0.25 mmol, 1 equiv.) and KSeCN (40 mg, 0.275 mmol, 1.1 equiv.), whereupon EtOAc (2 mL) was added and the resulting mixture was heated to 80 °C and stirred for 24 h. The mixture was then concentrated under a reduced pressure at 45 °C and pyridine (60 μ L, 3 equiv.) in HFIP (1.5 mL) was added to the formed residue. The resulting mixture was heated at 80 °C for 24 h until the full conversion of arylselenocyanate (monitored by TLC with 8:2, v/v, hexane: EtOAc was used as eluent). The reaction mixture was then diluted with water (10 mL) and the product was extracted by dichloromethane (3 \times 10 mL). Organic layers were combined, dried over Na₂SO₄, and concentrated under a reduced pressure at 45 °C. Selenes **2** were isolated by flash column chromatography (hexane:EtOAc 9:1, v/v).

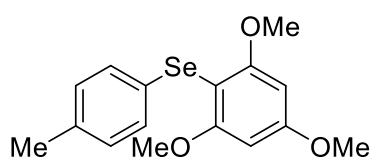


Phenyl(2,4,6-trimethoxyphenyl)selane (2a).⁶⁴ The reaction of phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1a** (0.25 mmol, 121 mg) according to general procedure **GP1** afforded

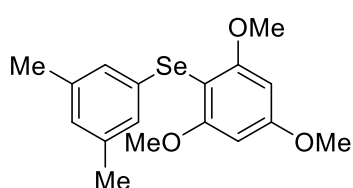
58 mg (73%) of **2a** isolated as the colorless crystalline solid; mp 105–107 °C (lit. yellow oil³²).

¹H NMR (400 MHz, CDCl₃) δ 7.19–7.08 (m, 5H), 6.21 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H).

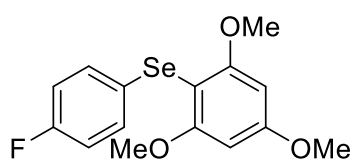
¹³C{¹H} (100 MHz, CDCl₃) δ 163.1, 162.0, 133.7, 128.8, 125.4, 97.1, 91.2, 56.4, 55.5.



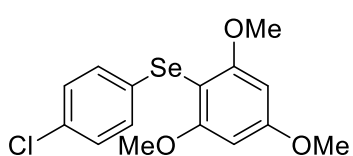
***p*-Tolyl(2,4,6-trimethoxyphenyl)selane (2b).**⁶⁴ The reaction of *p*-tolyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1b** (0.25 mmol, 125 mg) according to general procedure **GP1** afforded 32 mg (37%) of **2b** isolated as colorless oil (lit.⁶⁴ yellow oil). ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 6.8 Hz, 2H), 6.94 (d, *J* = 6.8 Hz, 2H), 6.19 (s, 2H), 3.85 (s, 3H), 3.78 (s, 6H), 2.24 (s, 3H). ¹³C{¹H} (100 MHz, CDCl₃) δ 162.9, 162.0, 135.2, 129.7, 129.6, 129.3, 97.7, 91.2, 56.4, 55.5, 21.1.



(3,5-Dimethylphenyl)(2,4,6-trimethoxyphenyl)selane (2c). The reaction of (3,5-dimethylphenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1c** (0.25 mmol, 128 mg) according to general procedure **GP1** afforded 32 mg (26%) of **2c** isolated as a colorless solid; mp 102–104 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.80 (s, 2H), 6.71 (s, 1H), 6.20 (s, 2H), 3.87 (s, 3H), 3.79κ (s, 6H), 2.19 (s, 3H). ¹³C{¹H} (100 MHz, CDCl₃) δ 162.9, 162.1, 138.2, 133.1, 127.4, 126.5, 91.3, 56.4, 21.4. HRMS (APCI) *m/z* calcd. for [M+H]⁺ C₁₇H₂₁O₃Se⁺: 353.0656, found 353.0651.

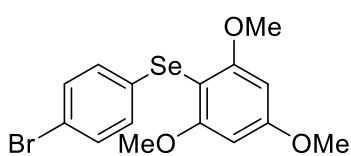


(4-Fluorophenyl)(2,4,6-trimethoxyphenyl)selane (2d). The reaction of (4-fluorophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1d** (0.25 mmol, 126 mg) according to general procedure **GP1** afforded 34 mg (40%) of **2d** isolated as the colorless solid; mp 80–81 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.22–7.17 (m, 2H), 6.85 (t, *J* = 8.8 Hz, 2H), 6.19 (s, 2H), 3.86 (s, 3H), 3.79 (s, 6H). ¹³C{¹H} (100 MHz, CDCl₃) δ 163.1, 162.8, 161.8, 160.3, 131.2 (d, *J*_{C-F} = 7 Hz), 127.8 (d, *J*_{C-F} = 3 Hz), 115.9 (d, *J*_{C-F} = 21 Hz), 97.7, 91.2, 56.4, 55.5. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -117.7. HRMS (APCI) *m/z* calcd. for [M+H]⁺ C₁₅H₁₆FO₃Se⁺: 343.0249, found 343.0245.



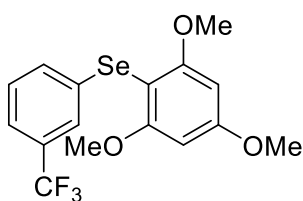
(4-Chlorophenyl)(2,4,6-trimethoxyphenyl)selane (2e). The reaction of (4-chlorophenyl)(2,4,6-trimethoxyphenyl)iodonium

trifluoroacetate **1e** (0.25 mmol, 130 mg) according to general procedure **GP1** afforded 50 mg (57%) of **2e** isolated as the colorless solid; mp 92–94 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.04 (s, 2H), 3.81 (s, 3H), 3.68 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.3, 161.9, 141.0, 131.8, 128.1, 124.4, 110.6, 91.4, 56.1, 55.7. HRMS (APCI) *m/z* calcd. for [M+H]⁺ C₁₅H₁₆ClO₃Se⁺: 358.9953, found 358.9946.



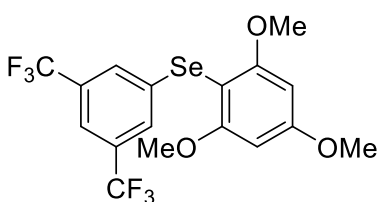
(4-Bromophenyl)(2,4,6-trimethoxyphenyl)selane (2f).⁶⁴ The

reaction of (4-bromophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1f** (0.25 mmol, 141 mg) according to general procedure **GP1** afforded 69 mg (68%) of **2f** isolated as a colorless solid; mp 108–109 °C from hexane: EtOAc (mp lit.³² 100–102 °C from hexane: EtOAc). ¹H NMR (400 MHz, CDCl₃) δ 7.61–7.55 (m, 4H), 6.04 (s, 2H), 3.81 (s, 3H), 3.67 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.3, 161.9, 141.0, 131.8, 128.1, 124.4, 110.6, 91.4, 56.1, 55.7.



(3-Trifluoromethylphenyl)(2,4,6-trimethoxyphenyl)selane (2g).

The reaction of (3-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1g** (0.25 mmol, 138 mg) according to general procedure **GP1** afforded 24 mg (23%) of **2g** isolated as a colorless solid; mp 113–114 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), 7.33 (d, *J* = 7.6 Hz 2H), 7.23 (t, *J* = 7.8 Hz 1H), 6.22 (s, 2H), 3.89 (s, 3H), 3.79 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.5, 161.9, 135.0, 131.9 (d, *J*_{C-F} = 1.1 Hz), 131.0 (q, *J*_{C-F} = 31.8 Hz), 128.9, 125.5 (q, *J*_{C-F} = 3.8 Hz), 124.0 (q, *J*_{C-F} = 271.0 Hz), 122.1 (q, *J*_{C-F} = 3.7 Hz), 96.1, 91.3, 56.4, 55.6. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –62.7. HRMS (APCI) *m/z* calcd. for [M+H]⁺ C₁₆H₁₆F₃O₃Se⁺: 393.0217, found 393.0212.

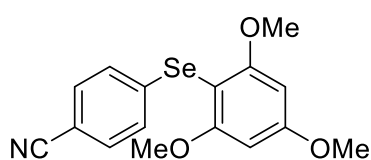


(3,5-Bis(trifluoromethyl)phenyl)(2,4,6-

trimethoxyphenyl)selane (2h). The reaction of (3,5-

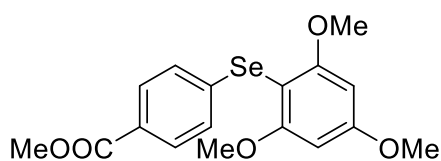
bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1h** (0.25 mmol, 155 mg) according to general procedure **GP1** afforded 62 mg

(54%) of **2h** isolated as the light yellow solid; mp 103–104 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (s, 3H), 6.23 (s, 2H), 3.89 (s, 3H), 3.80 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.9, 161.8, 137.0, 131.6 (q, *J*_{C-F} = 32.8 Hz), 128.5 (m), 123.3 (q, *J*_{C-F} = 271.3 Hz), 119.0 (m), 94.9, 91.4, 56.3, 55.6. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -63.0. HRMS (APCI) *m/z* calcd. for [M+H]⁺ C₁₅H₁₆NO₅Se⁺: 461.0091, found 461.0088.



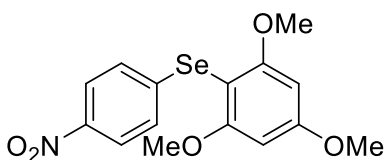
4-((2,4,6-Trimethoxyphenyl)selanyl)benzonitrile (2i). The

reaction of (4-cyanophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1i** (0.25 mmol, 127 mg) according to general procedure **GP1** afforded 73 mg (83%) of **2i** isolated as a pale yellow solid; mp 128–130 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.79 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.8, 162.0, 142.4, 132.1, 128.2, 119.4, 108.2, 95.0, 91.3, 56.4, 55.6. HRMS (APCI) *m/z* calcd. for [M+H]⁺ C₁₆H₁₆NO₃Se⁺: 350.0295, found 350.0291.



Methyl 4-((2,4,6-trimethoxyphenyl)selanyl)benzoate (2j).

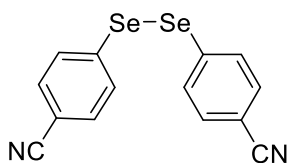
The reaction of (4-(methoxycarbonyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1j** (0.25 mmol, 136 mg) according to general procedure **GP1** afforded 73 mg (76%) of **2j** isolated as a colorless solid; mp 125–127 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.23 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.79 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.3, 163.5, 162.0, 141.6, 129.8, 127.7, 126.9, 95.7, 91.3, 56.4, 55.6, 52.1, 29.8. HRMS (ESI) *m/z* calcd. for [M+H]⁺ C₁₆H₁₆NO₃Se⁺: 383.0398, found 383.0392.



(4-Nitrophenyl)(2,4,6-trimethoxyphenyl)selane (2k). The

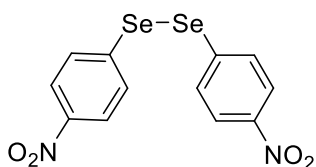
reaction of (4-nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate **1k** (0.25 mmol, 132 mg) according to general procedure **GP1** afforded 85 mg (92%) of **2k** isolated as a bright yellow solid; mp 134–135 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 9.2 Hz, 2H), 7.21 (d, *J* = 9.2 Hz, 2H), 6.24 (s, 2H),

3.90 (s, 3H), 3.80 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 163.9, 162.0, 145.5, 127.9, 123.7, 94.9, 91.3, 56.5, 55.7. HRMS (APCI) m/z calcd. for $[\text{M}+\text{H}]^+$ $\text{C}_{15}\text{H}_{16}\text{NO}_5\text{Se}^+$: 370.0194, found 370.0189.



4,4'-Diselanediyldibenzonitrile (3a).⁶⁵ The reaction of (4-cyanophenyl)(2,4-dimethoxyphenyl)iodonium trifluoroacetate **1m** (0.25 mmol, 120 mg) according to general procedure **GP1** afforded

34 mg (76%) of **3a** isolated as a brown solid; mp 152–154 °C (mp lit.⁶⁵ 156–158 °C). ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.0$ Hz, 4H), 7.54 (d, $J = 8.0$ Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100MHz, CDCl_3) δ 136.5, 132.8, 130.6, 118.3, 111.5.



1,2-Bis(4-nitrophenyl)diselane (3b).⁶⁶ The reaction of (4-nitrophenyl)(2,4-dimethoxyphenyl)iodonium trifluoroacetate **1n** (0.25 mmol, 125 mg) according to general procedure **GP1** afforded

45 mg (89%) of **3b** isolated as a brown solid; mp 179–181 °C (mp lit.⁶⁶ 179–180 °C). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.8$ Hz, 4H), 7.75 (d, $J = 8.8$ Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.5, 138.7, 130.5, 124.4.

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