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Metal-Free *ipso*-Selenocyanation of Arylboronic Acids Using Malononitrile and Selenium Dioxide

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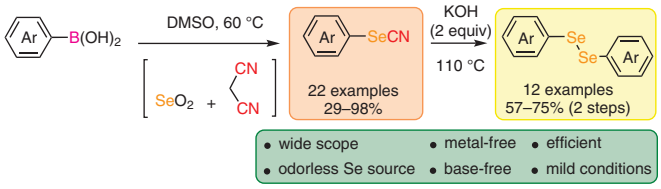

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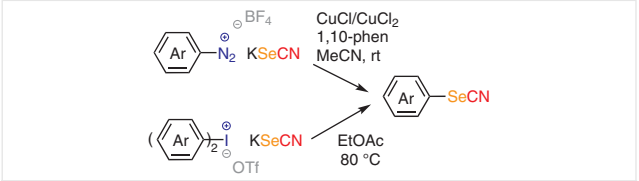
Abstract The first *ipso*-selenocyanation of arylboronic acids is achieved using selenium dioxide and malononitrile under mild conditions. The reaction is successful even without metal or base in DMSO. The major advantages of this new method are an easy set-up, excellent yields, and the use of odorless and inexpensive selenium reagents. Basic conditions subsequently afford new access to diaryldiselenides in good yields without isolating the organoselenocyanate intermediates.

Key words selenocyanate, arylboronic acid, selenium dioxide, malononitrile, diaryldiselenide

Recently, organic selenocyanates (RSeCN) have attracted the interest of medicinal chemists due to their remarkable biological activities especially as leishmanicidal[1] and cancer-chemopreventive agents.[2] The selenocyanate group is also studied for its synthetic usefulness as an air- and moisture-stable selenium halide analogue. Decyanation of selenocyanates via a reductant or a base, leads to the corresponding selenolate, which reacts with a large panel of electrophiles to give selenoether derivatives.[3] Another noteworthy example of decyanation recently gave the radical selenium intermediate.[3b] Thus, there is clear interest in new methodologies involving the SeCN group.

Various strategies involving the selenocyanate group have been developed on electron-rich heterocycles.[4] However, only a few approaches are applied to non-activated aryls. The selenocyanation of aryldiazonium tetrafluoroborates with potassium selenocyanate is one example (Scheme 1).[5] To obtain good yields, catalytic quantities of $CuCl/CuCl_2$ and phenanthroline are required to perform this Sandmeyer reaction. Lately, more electrophilic diaryliodonium salts have been used with KSeCN for the selenocyanation of aryl compounds.[6]

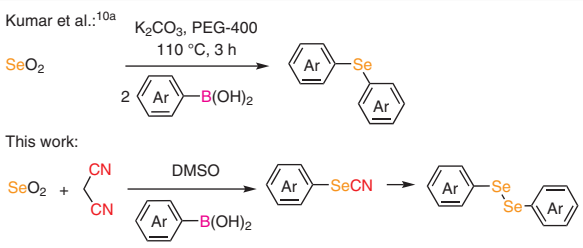


Scheme 1 Selenocyanation of non-activated aryls

However, these procedures have several drawbacks: use of non-stable diazoniums, high quantities of metals/ligand, or formation of stoichiometric amount of iodide side product.

Over past decades, the transition-metal-free *ipso*-functionalization of arylboronic acids has attracted interest as a powerful tool to form carbon–heteroatom bonds (C–X) in aromatic compounds.[7] For example, no requirement for any metal or base was reported for the *ipso*-halogenation of arylboronic acids with highly electrophilic *N*-halosuccinimides (NBS,[8a] NIS,[8b] or Selectfluor[8c]) in acetonitrile. In contrast, *ipso*-thiocyanations require base and $Cu(OAc)_2$ to perform the reaction from KSCN.[9]

For *ipso*-selenations, an eco-friendly and metal-free protocol was developed to synthesize diarylselenides from arylboronic acids and electrophilic SeO_2 (Scheme 2).[10]



Scheme 2 *ipso*-Selenation of arylboronic acids

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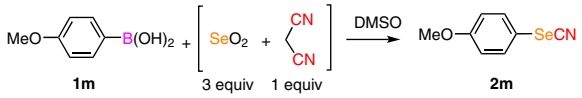
Triselenodicyanide [$Se(SeCN)_2$][11,12] represents an ideal electrophilic source for the selenocyanation of activated nitrogen- or oxygen-containing heterocycles.[13] Its preparation from malononitrile and odorless selenium dioxide is simple and fast. In this study, we further investigated the reactivity of arylboronic acids with triselenodicyanide.

To evaluate the reactivity of arylboronic acids a detailed optimization study was performed as summarized in Table 1. First, a solution of electrophilic triselenodicyanate was prepared mixing selenium dioxide (3 equiv) and malononitrile (1 equiv) in wet DMSO (1 mol·L^{-1}) for 30 minutes.[13] The reaction was performed in an open-air system to release the generated gas.[11]

Table 1 Optimization of Reaction Conditions[a]



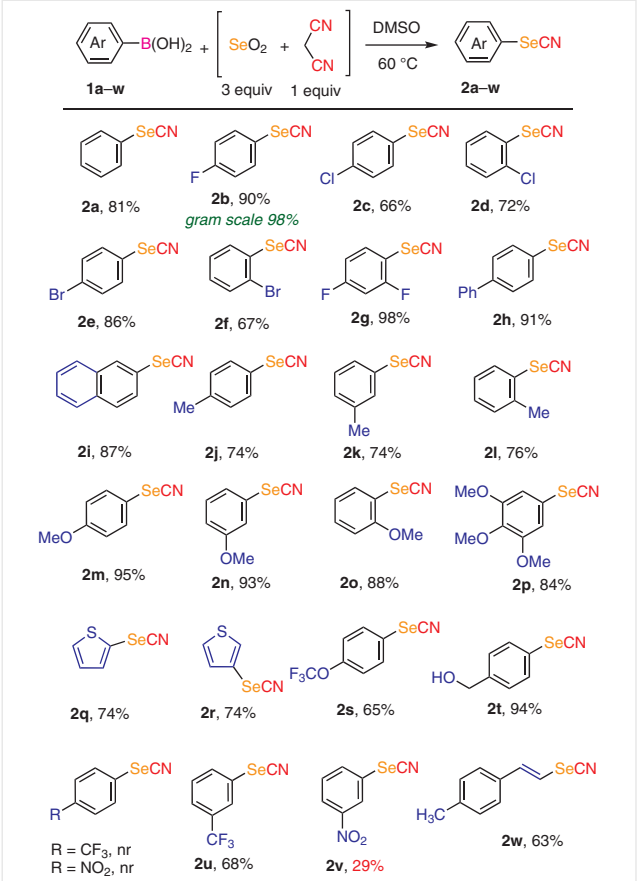
1m — 3 equiv — 1 equiv — 2m

Entry	Solvent	Conditions	Yield (%)[b] of **2m**
1	wet DMSO	25 °C, 24 h	n.r.
2	wet DMSO	40 °C, 24 h	43
3	**wet DMSO**	**60 °C, 14 h**	**95**
4	wet DMSO	60 °C, 6 h	73
5	anhyd DMSO	60 °C, 14 h	74
6	wet DMF	60 °C, 14 h	56
7	EtOH	60 °C, 14 h	17
8	DMSO/H_2O 95/5	60 °C, 14 h	84
9	DMSO/H_2O 90/10	60 °C, 14 h	93
10	DMSO/H_2O 80/20	60 °C, 14 h	79
11	H_2O	60 °C, 14 h	n.r.

[a] Reaction conditions: 4-methoxyphenylboronic acid (1 mmol, 1 equiv) was added to a prepared solution of malononitrile (1 equiv) and SeO_2 (3 equiv) in solvent (1 M). The reaction mixture was stirred at 60 °C for 14 h.
[b] Isolated yield; n.r.: no reaction (recovered starting material).

Then, 4-methoxyphenylboronic acid **1m** was added as a model substrate (Table 1, entry 1). Temperature evaluation revealed no reaction after 24 hours at room temperature (entry 1). Raising the temperature to 40 °C led to the formation of the desired selenocyanate **2m** without need for any metal or base. However, the yield from selenocyanation was only moderate even after 24 hours (entry 2, 43%). In these conditions, no secondary compound such as Ar_2Se or Ar_2Se_2 derivative was observed. Raising the temperature to 60 °C dramatically increased the yield to 95% (entry 3). Attempting to reduce the reaction time resulted in lower yields (entry 4). The yield was also lower in anhydrous DMSO (entry 5) or other solvents (DMF, EtOH) (entries 6, 7), probably due to the poor solubility of SeO_2 in these solvents. To examine the role of water, we determine that the optimized proportion of water in anhydrous DMSO should be 10% v/v. (entries 8–10). In water, no reaction occurred, owing to the weak stability of the triselenodicyanide under hydrolysis (entry 11).

Next, we examined the scope of our selenocyanation method with a large number of arylboronic acids (Scheme 3). In most cases, selenocyanation resulted in moderate to excellent yields with arylboronic acids bearing either electron-rich or -deficient substituents (**2a–t**). The relative position of the substituent on the aromatic ring (*ortho*, *meta*-, or *para*) did not affect the efficiency of the reaction. Selenocyanation resulted in moderate yields with methyl substituents **2j**, **2l** and excellent yields with methoxy substituents **2m–p**. Both *ortho*- and *para*-halogen substituents were well tolerated, with higher yields observed for Br and F derivatives. Arylboronic acids with trifluoromethoxy (**2s**) or alcohol (**2t**) substituent on the phenyl ring were also well tolerated. With a strongly deactivating CF_3 or NO_2 group in *para*-position, no reaction occurred; however, when it was in *meta*-position, moderate yields were observed (**2u**, *m*-CF_3, 68%) (**2v**, *m*-NO_2, 29%). *para*-Phenyl-substituted arylbo-

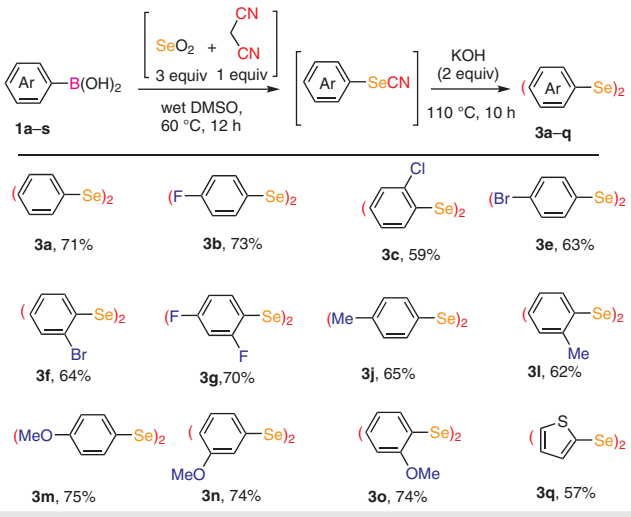


Scheme 3 Scope of the *ipso*-selenocyanation of arylboronic acids. *Reagents and conditions*: arylboronic acid **1** (1 mmol, 1 equiv) was added to a pre-prepared solution of malononitrile (1 equiv) and SeO_2 (3 equiv) in DMSO (1 M). The reaction mixture was stirred at 60 °C for 14 h. Isolated yields are shown; n.r.: no reaction.

ronic acids **1h** and naphthyl **1i** successfully gave the biaromatic selenocyanate compound **2h** and **2i** in 91% and 87% yield, respectively. Fused rings worked well with naphthyl aromatic **2i**. Heterocycles such as 2-thiophene **2q** (74%) or 3-thiophene **2r** (74%) rings were compatible with selenocyanation. Finally, vinyl selenocyanate **2w** was obtained from *trans*-2-(4-methylphenyl)vinylboronic acid in 63% yield without modifying the double bond *E*-configuration. In some cases, traces of protodeboronated products were also observed.

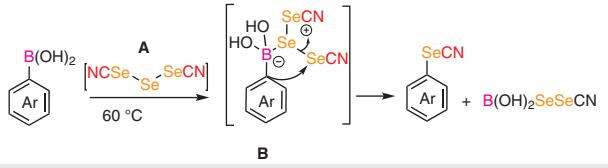
A gram-scale reaction demonstrated the performance of the preparative applications. Reaction of 4-fluorophenylboronic acid (**1b**; 16 mmol, 2.24 g) afforded 4-fluorophenylselenocyanatobenzene **2b** in high yield (98%, 3.13 g).

To demonstrate the usefulness of these selenocyanated derivatives, we explored their transformation into valuable diselenide compounds, commonly used as a starting material in various applications. We first attempted decyanation under basic conditions,[14] followed by oxidation in air in a one-pot sequential process. Unfortunately, no reaction occurred with one equivalent of potassium hydroxide at 60 °C. A brief optimization showed that two equivalents of KOH and heating to 110 °C were required for complete conversion into diaryldiselenide **3a** (Scheme 4). These drastic conditions were attributed to the lower solubility of KOH in DMSO; nonetheless, diselenides **3a–q** were isolated in good yields (57–74%). The principal contribution of this new methodology lies in forming the diselenide (ArSeSeAr) alone with no trace of the monoselenide compound (ArSeAr). Diarylmonoselenide was often observed as a side product in previously reported methodologies, involving tedious separation from diaryldiselenide.



Scheme 4 Synthesis of diaryldiselenide compounds **3a–q** from arylboronic acids under basic conditions

Based on the literature, a plausible reaction mechanism is suggested in Scheme 5. Initially, the triselenodicyanide intermediate **A** is produced from malononitrile and selenium dioxide in DMSO.[11] In the presence of arylboronic acid, the triselenodicyanide could form complex **B**. Then the nucleophilic aryl ring of the arylboronic acid could add on to the electrophilic SeCN group to give the arylselenocyanate compound.



Scheme 5 Proposed mechanism for the *ipso*-selenocyanation of arylboronic acids with triselenodicyanide in DMSO

In summary, we have developed the first methodology for the *ipso*-selenocyanation of arylboronic acids. The reaction is easy to set-up under mild conditions and affords a wide variety of arylselenocyanate compounds in good yields. The absence of metal or base, the use of an odorless selenium source, and the gram scale-up make this new approach very attractive. Further transformation into diaryldiselenides is easy under basic conditions and in a one-pot sequential process. Consequently, these two methods represent a robust protocol for the synthesis of a large panel of arylselenocyanate or diaryldiselenide compounds.

Melting points were determined on a Büchi B-540 apparatus and are uncorrected. ^{1}H NMR (300 or 400 MHz, reference $CDCl_3$ δ = 7.26 ppm) were recorded on Bruker Avance III nanobay at the Faculté des Sciences et Techniques de Saint-Jérôme, Marseille and ^{13}C NMR spectra (62.9 MHz, reference $CDCl_3$ δ = 77.16 ppm) were recorded on a Bruker ARX 200 spectrometer at the Faculté de Pharmacie, Marseille. Silica gel 60 (Merck, particle size 0.063–0.200 mm, 70–230 mesh ASTM) was used for the purifications by column chromatography. TLC was performed on 5 cm × 10 cm aluminum plates coated with silica gel 60F-254 (Merck) using an appropriate eluent. Petroleum ether (PE) used in this study refers to the fraction boiling in the range 40–65 °C. HRMS spectra were recorded on QStar Elite (Applied Biosystems SCIEX) spectrometer at the Spectropole, Faculté des Sciences et Techniques de Saint-Jérôme, Marseille with PEG as the matrix.

Selenocyanates 2a–w; General Procedure

To a solution of SeO_2 (333 mg, 3 mmol, 3 equiv) in wet DMSO (1 mL) was added malononitrile (66 mg, 1 mmol, 1 equiv). The solution was stirred at rt for 30 min, then arylboronic acid **1** (1 mmol, 1 equiv) was added. The mixture was heated at 60 °C for 14 h. After cooling to rt, H_2O (10 mL) was added. The resulting mixture was extracted with DCM (3 × 10 mL) and the combined organic layers were dried (Na_2SO_4), filtered, and reduced under vacuum. The crude product was purified by column chromatography (PE/DCM 80/20) to yield the desired arylselenocyanate **2**.

Selenocyanatobenzene (2a)[6]

Yellow oil; yield: 146 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.62 (m, 2 H), 7.45–7.37 (m, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 132.9 (2 × CH), 130.5 (2 × CH), 129.9 (CH), 121.9 (C), 101.6 (CN).

1-Fluoro-4-selenocyanatobenzene (2b)

Yellow oil; yield: 178 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.64 (d, *J* = 8.9, 5.0 Hz, 2 H), 7.13–7.09 (dd, *J* = 8.8, 8.4 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 163.9 (d, $^1J_{C,F}$ = 251.8 Hz, CF), 135.9 (d, $^3J_{C,F}$ = 8.5 Hz, CH), 117.8 (d, $^2J_{C,F}$ = 22.4 Hz, CH), 116.2 (d, $^4J_{C,F}$ = 3.5 Hz, Cq), 101.4 (CN).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –113.04 (s, 1 F).

HRMS (ESI+): *m*/*z* calcd for $[C_7H_4FNSe + Ag]^+$: 307.8538; found: 307.8534.

1-Chloro-4-selenocyanatobenzene (2c)[6]

White solid; yield: 144 mg (66%); mp 35–36 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 6.7 Hz, 2 H), 7.39 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.6 (Cq), 136.6 (2 × CH), 130.7 (2 × CH), 119.8 (Cq), 101.0 (CN).

1-Chloro-2-selenocyanatobenzene (2d)

White solid; yield: 174 mg (72%); mp 38–39 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.76 (m, 1 H), 7.43–7.40 (m, 1 H), 7.35–7.33 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 132.5 (C), 130.9 (CH), 130.0 (CH), 130.0 (CH), 128.9 (CH), 124.2 (C), 101.0 (CN).

HRMS (ESI+): *m*/*z* calcd for $[C_7H_4ClNSe + Ag]^+$: 323.8243; found: 323.7244.

1-Bromo-4-selenocyanatobenzene (2e)[6]

White solid; yield: 223 mg (86%); mp 70–71 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.49 (m, 4 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 134.7 (2 × CH), 134.0 (2 × CH), 125.0 (C), 120.9 (C), 101.2 (CN).

1-Bromo-2-selenocyanatobenzene (2f)[6]

White solid; yield: 173 mg (67%); mp 47–48 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.55 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.40 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.25 (dd, *J* = 7.7, 1.5 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 133.1 (CH), 130.7 (CH), 130.0 (CH), 129.5 (CH), 126.8 (C), 121.8 (C), 101.7 (CN).

2,4-Difluoro-1-selenocyanatobenzene (2g)

White solid; 211 mg (98%); mp 32–33 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.68 (m, 1 H), 7.01–6.96 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 164.7 (dd, *J* = 254.3, 11.1 Hz, Cq), 161.3 (dd, *J* = 250.3, 11.5 Hz, Cq), 135.9 (dd, *J* = 10.7, 2.7 Hz, CH), 113.8 (dd, *J* = 22.1, 3.6 Hz, CH), 105.5 (dd, *J* = 26.1, 26.0 Hz, CH), 104.0 (dd, *J* = 22.1, 4.1 Hz, Cq), 99.7 (CN).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –104.88, –97.22.

HRMS (ESI+): *m*/*z* calcd for $[C_7H_3F_2NSe + Ag]^+$: 325.8446; found: 325.8440.

4-Selenocyanato-1,1′-biphenyl (2h)[15a]

White solid; yield: 233 mg (91%); mp 94–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 7.1 Hz, 2 H), 7.49 (d, *J* = 7.6 Hz, 2 H), 7.41 (dd, *J* = 8.0 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 143.1 (C), 139.5 (C), 133.4 (2 × CH), 129.1 (2 × CH), 128.3 (CH), 127.2 (2 × CH), 120.5 (C), 101.6 (CN).

2-Selenocyanatonaphthalene (2i)[6,15a]

White solid; yield: 203 mg (87%); mp 61–62 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.85 (d, *J* = 8.7 Hz, 2 H), 7.81 (dd, *J* = 6.1, 3.2 Hz, 1 H), 7.64 (d, *J* = 8.6, 1.7 Hz, 1 H), 7.56 (d, *J* = 5.8, 2.8 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 134.0 (C), 133.3 (C), 132.7 (CH), 130.3 (CH), 128.9 (CH), 128.1 (CH), 127.8 (2 × CH), 127.5 (CH), 118.9 (C), 101.6 (CN).

1-Methyl-4-selenocyanatobenzene (2j)[6]

Yellow oil; yield: 143 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 2.37 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 140.4 (C), 133.3 (2 × CH), 131.1 (2 × CH), 117.9 (C), 101.9 (CN), 21.2 (CH_3).

1-Methyl-3-selenocyanatobenzene (2k)

Yellow oil; yield: 142 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 1 H), 7.21–7.30 (m, 2 H), 2.37 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 140.8 (C), 133.4 (CH), 130.7 (CH), 130.2 (CH), 129.8 (CH), 121.6 (C), 101.7 (CN), 21.4 (CH_3).

HRMS (ESI+): *m*/*z* calcd for $[C_8H_7NSe + NH_4]^+$: 215.0077; found: 215.0082.

1-Methyl-2-selenocyanatobenzene (2l)

Yellow oil; yield: 148 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.1 Hz, 1 H), 7.37–7.29 (m, 2 H), 7.23 (dd, *J* = 7.4, 6.5 Hz, 1 H), 2.50 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 140.0 (C), 134.0 (CH), 131.3 (CH), 130.4 (CH), 127.9 (CH), 123.1 (C), 101.3 (CN), 22.4 (CH_3).

HRMS (ESI+): *m*/*z* calcd for $[C_8H_7NSe + Na]^+$: 219.9636; found: 219.9634

1-Methoxy-4-selenocyanatobenzene (2m)[6]

Yellow oil; yield: 200 mg (95%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.1 Hz, 2 H), 6.91 (d, *J* = 8.1 Hz, 2 H), 3.83 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 161.5 (C), 136.2 (2 × CH), 116.1 (2 × CH), 111.2 (CH), 102.2 (CN), 55.6 (OCH_3).

1-Methoxy-3-selenocyanatobenzene (2n)

Yellow oil; yield: 197 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.16 (m, 2 H), 6.94 (dd, *J* = 8.3, 2.4 Hz, 1 H), 3.83 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 160.5 (C), 131.1 (CH), 124.6 (CH), 122.4 (C), 117.8 (CH), 115.7 (CH), 101.5 (CN), 55.5 (OCH_3).

HRMS (ESI+): *m*/*z* calcd for [C_8H_7NOSe + Na]$^+$: 235.9585; found: 235.9583.

1-Methoxy-2-selenocyanatobenzene (2o)

Colorless oil; yield: 187 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.35 (dd, *J* = 8.2, 1.5 Hz, 1 H), 7.03 (dd, *J* = 7.7, 1.1 Hz, 1 H), 6.90 (d, *J* = 8.2 Hz, 1 H), 3.90 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 155.9 (C), 130.2 (CH), 130.0 (CH), 122.9 (CH), 112.7 (C), 111.1 (CH), 101.4 (CN), 56.3 (OCH_3).

HRMS (ESI+): *m*/*z* calcd for [C_8H_7NOSe + Na]$^+$: 235.9585; found: 235.9584.

1,2,3-Trimethoxy-5-selenocyanatobenzene (2p)

Yellow oil; yield: 229 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (s, 2 H), 3.9 (s, 6 H), 3.8 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 154.2 (CH), 139.7 (C), 115.0 (C), 110.9 (2 × CH), 101.7 (C), 61.0 (CH_3), 56.5 (2 × CH_3).

HRMS (ESI+): *m*/*z* calcd for [$C_{10}H_{12}NO_3Se$ + H]$^+$: 273.9977; found: 273.9978.

2-Selenocyanatothiophene (2q)

Yellow oil; yield: 141 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 5.5, 1.25 Hz, 1 H), 7.46 (dd, *J* = 3.5, 1.0 Hz, 1 H), 7.08 (dd, *J* = 5.2, 3.5 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 139.1 (CH), 134.7 (CH), 128.8 (CH), 112.5 (C), 101.1 (CN).

HRMS (ESI+): *m*/*z* calcd for [C_5H_3NSSe + Na]$^+$: 211.9044; found: 211.90421.

3-Selenocyanatothiophene (2r)

Yellow oil; yield: 139 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.45 (d, *J* = 5.2, 3.0 Hz, 1 H), 7.75 (dd, *J* = 5.0, 1.2 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 131.6 (CH), 131.5 (CH), 128.3 (CH), 112.1 (C), 101.1 (CN).

HRMS (ESI+): *m*/*z* calcd for [C_5H_3NSSe + Na]$^+$: 211.9044; found: 211.9041.

1-Selenocyanato-4-(trifluoromethoxy)benzene (2s)

Yellow solid; yield: 173 mg (65%); mp 43–44 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.9 Hz, 1 H), 7.97 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.4 (C), 134.7 (2 × CH), 122.7 (2 × CH), 120.3 (q, $^1J_{C,F}$ = 258.7 Hz, CF_3), 119.8 (C), 101.0 (CN).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –57.91 (s, 3 F).

HRMS (ESI+): *m*/*z* calcd for [$C_8H_4F_3NOSe$ + Na]$^+$: 289.9303; found: 289.9299.

(4-Selenocyanatophenyl)methanol (2t)

White solid; yield: 200 mg (94%); mp 52–53 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.2 Hz, 2 H), 7.41 (d, *J* = 8.1 Hz, 2 H), 4.73 (s, 2 H), 1.78 (s, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 143.2 (C), 133.1 (2 × CH), 128.6 (2 × CH), 120.3 (C), 101.9 (CN), 64.1 (CH_2).

HRMS (ESI+): *m*/*z* calcd for [C_8H_7NOSe + NH_4]$^+$: 231.0031; found: 231.0030.

1-Selenocyanato-3-(trifluoromethyl)benzene (2u)

White solid; yield: 170 mg (68%); mp 28–29 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.85 (d, *J* = 7.9 Hz, 2 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 7.57 (dd, *J* = 7.8, 7.9 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 135.9 (CH), 132.7 (q, $^2J_{C,F}$ = 33.3 Hz, C), 131.0 (CH), 129.2 (q, $^3J_{C,F}$ = 3.8 Hz, CH), 126.7 (q, $^3J_{C,F}$ = 3.6 Hz, CH), 123.1 (q, $^1J_{C,F}$ = 272.9 Hz, C), 123.0 (C), 100.6 (CN).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.91 (s, 3 F).

HRMS (ESI+): *m*/*z* calcd for [$C_8H_4F_3NSe$ + Ag]$^+$: 357.8509; found: 357.8510.

1-Nitro-3-selenocyanatobenzene (2v)

Orange solid; yield: 66 mg (29%); mp 58–59 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (dd, *J* = 1.8, 1.8 Hz, 1 H), 8.30 (dd, *J* = 8.3, 0.9 Hz, 1 H), 8.00 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.65 (dd, *J* = 8.1, 8.0 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 148.9 (C), 138.1 (CH), 131.4 (CH), 127.1 (CH), 124.7 (CH), 123.8 (C), 100.1 (CN).

HRMS (ESI+): *m*/*z* calcd for [$C_7H_4N_2O_2Se$ + Ag]$^+$: 334.8485; found: 334.8489.

(*E*)-1-Methyl-4-(2-selenocyanatovinyl)benzene (2w)[3b]

White solid; yield: 140 mg (63%); mp 65 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.1 Hz, 2 H), 7.10–7.19 (m, 3 H), 6.79 (d, *J* = 15.3 Hz, 1 H), 2.36 (s, CH_3, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 142.1 (CH), 139.8 (C), 132.5 (C), 129.8 (2 × CH), 126.9 (2 × CH), 105.9 (CH), 100.6 (CN), 21.5 (CH_3).

1,2-Diselanes 3a–c,e–g,j,l–o,q; General Procedure

To a solution of SeO_2 (333 mg, 3 mmol, 3 equiv) in wet DMSO (1 mL) was added malononitrile (66 mg, 1 mmol, 1 equiv). The solution was stirred at rt for 30 min, then arylboronic acid **1** (1 mmol, 1 equiv) was added. The mixture was heated at 60 °C for 10 h, then KOH (110 mg, 2 equiv) was added. The mixture was heated at 110 °C for 12 h. After cooling to rt, H_2O (10 mL) was added, and the resulting mixture was extracted with DCM (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and reduced under vacuum. The crude product was purified by column chromatography (PE/DCM 90:10) to afford the desired pure diselane compound **3**.

1,2-Bisphenyldiselane (3a)[15b]

Yellow solid; yield: 111 mg (71%); mp 62–63 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.60 (m, 1 H), 7.30–7.20 (m, 4 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 131.6 (2 × CH), 131.0 (C), 129.3 (2 × CH), 127.9 (CH).

1,2-Bis(4-fluorophenyl)diselane (3b)[15b]

Yellow oil; yield: 127 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.57 (m, 2 H), 6.95–7.00 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 163.1 (d, ^1J = 248.5 Hz, C), 134.9 (d, ^3J = 8.1 Hz, 2 × CH), 125.7 (d, ^4J = 3.4 Hz, Cq), 116.5 (d, $^2J_{C,F}$ = 21.8 Hz, 2 × CH).

^{19}F NMR (376 MHz, $CDCl_3$): δ = 112.4 (s, 1 F).

1,2-Bis(4-chlorophenyl)diselane (3c)[15b]

Yellow solid; yield: 112 mg (59%); mp 114–115 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.59 (m, 1 H), 7.35–7.27 (m, 1 H), 7.20–7.16 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 133.3 (C), 130.8 (CH), 129.4 (CH), 129.3 (C), 128.5 (CH), 128.0 (CH).

1,2-Bis(4-bromophenyl)diselane (3e)[15b]

Yellow oil; yield: 148 mg (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.6 Hz, 2 H), 7.21 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 133.6 (2 × CH), 132.5 (2 × CH), 129.6 (C), 122.6 (C).

1,2-Bis(2-bromophenyl)diselane (3f)[15c]

Yellow oil; yield: 150 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.9 Hz, 1 H), 7.49 (d, *J* = 7.8 Hz, 1 H), 7.22 (dd, *J* = 7.4 Hz, 1 H), 7.09 (dd, *J* = 7.5 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 132.7 (CH), 131.5 (C), 130.7 (CH), 128.7 (CH), 128.6 (CH), 123.0 (C).

1,2-Bis(2,4-difluorophenyl)diselane (3g)

Orange solid; yield: 134 mg (70%); mp 71–72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.21 (dd, *J* = 8.0, 7.2 Hz, 1 H), 6.87 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 3.91 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 164.0 (dd, *J* = 251.4, 11.1 Hz, Cq), 161.8 (dd, *J* = 247.4, 12.2 Hz, Cq), 136.6 (dd, *J* = 9.5, 3.7 Hz, CH), 112.5 (dd, *J* = 21.4, 3.7 Hz, CH), 112.3 (dd, *J* = 22.7, 4.0 Hz, Cq), 104.4 (dd, *J* = 25.7, 27.3 Hz, CH).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.1 (q, *J* = 8.4 Hz), –108.2 (t, *J* = 8.8 Hz).

HRMS (ESI+): *m*/*z* calcd for $[C_{12}H_6F_4Se_2 + Ag]^+$: 492.7781; found: 492.7779.

1,2-Di-*p*-tolyldiselane (3j)[15b]

Yellow oil; yield: 110 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 7.8 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 138.1 (C), 132.4 (2 × CH), 130.1 (2 × CH), 127.8 (C), 21.3 (CH_3).

1,2-Di-*o*-tolyldiselane (3l)[15b]

Orange oil; yield: 105 mg (62%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 1.8, 1.8 Hz, 1 H), 7.20–7.05 (m, 3 H), 2.44 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 138.9 (C), 132.7 (CH), 131.0 (C), 130.1 (CH), 128.1 (CH), 127.0 (CH), 22.3 (CH_3).

1,2-Bis(4-methoxyphenyl)diselane (3m)[15b]

Orange solid; yield: 140 mg (75%); mp 52–53 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.8 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 3.81 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 160.2 (C), 135.6 (2 × CH), 122.1 (C), 114.8 (2 × CH), 55.4 (OCH_3).

1,2-Bis(3-methoxyphenyl)diselane (3n)[15b]

Yellow solid; yield: 138 mg (74%); mp 192–193 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.10 (m, 3 H), 6.77 (m, 1 H), 3.77 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 159.9 (C), 131.9 (C), 130.0 (CH), 123.5 (CH), 116.6 (CH), 113.9 (CH), 55.3 (OCH_3).

1,2-Bis(2-methoxyphenyl)diselane (3o)[15b]

Yellow solid; 138 mg (74%); mp 91–92 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.21 (dd, *J* = 8.0, 7.2 Hz, 1 H), 6.87 (dd, *J* = 7.6, 7.6 Hz, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 3.91 (s, 3 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 157.0 (C), 130.8 (CH), 128.3 (CH), 122.0 (CH), 118.9 (C), 110.3 (CH), 56.1 (OCH_3).

1,2-Bis(thiophen-2-yl)diselane (3q)[15c]

Orange solid; yield: 92 mg (57%); mp 56–57 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 5.2 Hz, 1 H), 7.23 (d, *J* = 3.3 Hz, 1 H), 7.00 (dd, *J* = 5.2, 3.6 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 137.1 (CH), 133.1 (CH), 128.3 (CH), 125.8 (C).

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