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Syntheses of selenoesters through C–H selenation of aldehydes with diselenides under metal-free and solvent-free conditions†

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A DTBP-promoted C–H selenation of aldehydes with diselenides under metal-free and solvent-free conditions is described. This system shows good functional group compatibility, functional groups including bromo, trifluoromethyl, chloro, amine and heterocycle-containing moieties including thiophene and furan are all tolerated by the reaction conditions employed. Both diaryl and dialkyl diselenides reacted smoothly with aldehydes to provide selenoesters in good to excellent yields.

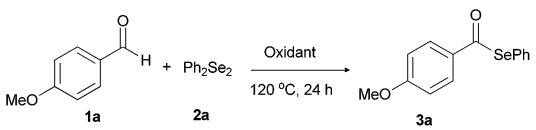
Introduction

Recently, organoselenium compounds have gained much attention due to their applications in the fields of chemical biology,[1] asymmetric catalysis,[2,3] cross-coupling reactions,[4] organic synthesis,[5–7] materials science,[8] and natural products.[9] Many methods have been reported for preparing selenoesters,[10–13] and the transition-metal-catalyzed cross-coupling reaction of acyl chlorides with nucleophilic selenium reagents is one of the most popular approaches for preparing such molecules.[12,13] Transition metals including Hg,[12a] Pd,[12d,13a] Fe,[12g] Sm,[13b] In,[12f,13c,13d] Rh,[13e] Cu,[13f] Zn,[13g] La[13h] have been used as the catalysts for this transformation. However, the above methods suffered from some synthetic drawbacks due to the issue of air stability and/or toxicity of the transition metals, starting materials and solvents; moreover, these systems usually used not easily available selenium containing precursors.[10a,12a,12d,14a] Recently, organo-catalysis[15] has been employed as an alternative choice to replace transition metal mediated transformations,[10] and application of this approach to the direct C–H bond selenation of aldehydes with diselenides has received less attention.[10c] Very recently, we have reported the DTBP-promoted cross-coupling of aldehydes with disulfides to provide thioesters under metal-free conditions.[15a] Here, we report that the selenoesters can be prepared through the coupling of aldehydes with diselenides in the presence of DTBP as an oxidant without transition metals under solvent-free conditions.

Results and discussion

Initially, 4-methoxybenzaldehyde (**1a**) and diphenyl diselenide (**2a**) were chosen as the coupling partners to determine the optimal reaction conditions. The results are summarized in Table 1. Only trace amount of the selenoester **3a** was obtained

Table 1 Optimization of the reaction conditions[a]



Entry	Oxidant (equiv.)	Yield[b] (%)
1[c]	TBHP (4.0)	Trace
2	TBPB (4.0)	64
3	BPO (4.0)	Trace
4	$K_2S_2O_8$ (4.0)	Trace
5	AcOOH (4.0)	N.R.
6	*m*-CPBA (4.0)	N.R.
7	H_2O_2 (4.0)	Trace
8	DTBP (4.0)	93
9	DTBP (3.0)	41
10	DTBP (2.0)	21
11[d]	DTBP (4.0)	31
12[e]	DTBP (4.0)	16
13[f]	DTBP (4.0)	68
14[g]	DTBP (4.0)	59
15[h]	DTBP (4.0)	68

[a] Reaction conditions: 4-methoxybenzaldehyde (1.0 mL), diphenyl diselenide (0.25 mmol) and oxidant (2.0 mmol) were reacted at 120 °C for 24 h. [b] Isolated yield based on diphenyl diselenide. [c] TBHP in water. [d] 110 °C. [e] 100 °C. [f] 16 h. [g] 0.5 mL of 4-methoxybenzaldehyde was used. [h] Reaction was carried out under microwave conditions for 30 min. (TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-butyl peroxybenzoate, BPO = benzoyl peroxide, AcOOH = peracetic acid, DTBP = di-*tert*-butyl peroxide).

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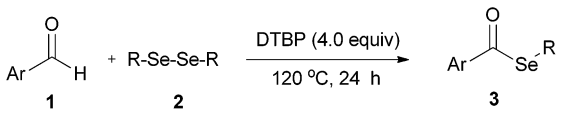
† Electronic supplementary information (ESI) available: NMR spectra of compounds **3a–r** and **4a–i**. See DOI: 10.1039/c4ra07983c

‡ Both authors contributed equally to this work.

Table 2 DTBP-promoted synthesis of selenoesters from diaryl diselenides and aldehydes[a]



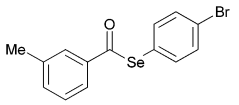
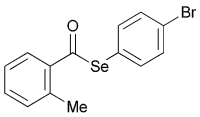
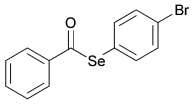
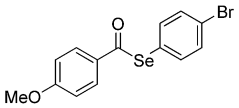
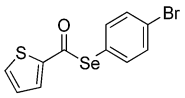
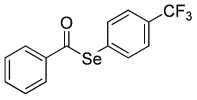
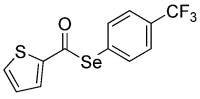
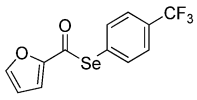
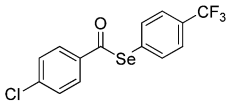
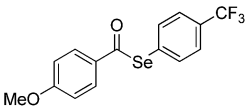
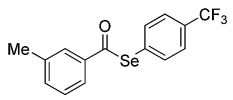
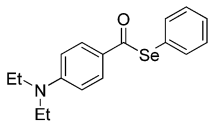
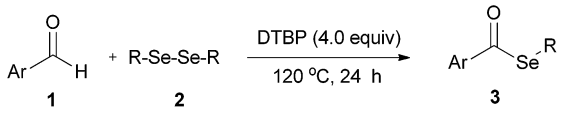
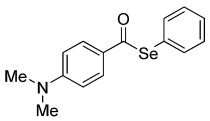
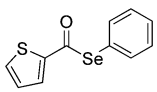
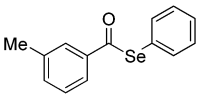
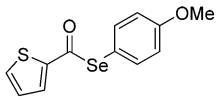
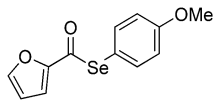
Entry	Product		Yield[b] (%)
1		**3b**	94
2		**3c**	88
3		**3d**	76
4		**3e**	62
5		**3f**	88
6		**3g**	78
7		**3h**	86
8		**3i**	74
9		**3j**	77
10		**3k**	59 (90)[c]
11		**3l**	52 (91)[c]
12		**3m**	79

Table 2 (*Contd.*)



Entry	Product		Yield[b] (%)
13		**3n**	60
14		**3o**	65
15		**3p**	92
16		**3q**	88
17		**3r**	72

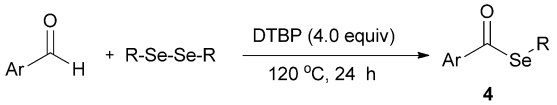
[a] Reaction conditions unless otherwise stated: aldehyde (1.0 mL), diaryl diselenide (0.25 mmol) and DTBP (2.0 mmol) were reacted at 120 °C for 24 h using Schlenk tube. [b] Isolated yields based on diselenides. [c] Reactions were carried out using sealed tube.

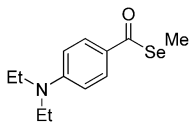
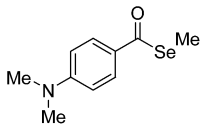
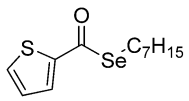
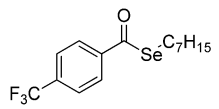
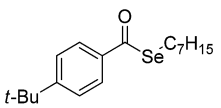
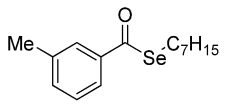
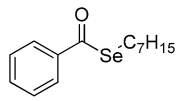
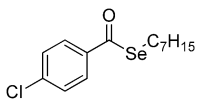
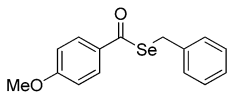
when the reaction was carried out by using TBHP (*tert*-butyl hydroperoxide) as an oxidant[14b] (Table 1, entry 1). Interestingly, a 64% yield of the target was obtained when the reaction was carried using TBPB (*tert*-butyl peroxybenzoate) as oxidant (Table 1, entry 2). Based on this result, we screened other oxidants (Table 1, entries 3–8), and DTBP was found to be the best, giving **3a** in 93% yield (Table 1, entry 8).[16] It was also found that lower amounts of DTBP (Table 1, entries 9 and 10), lower reaction temperatures (Table 1, entries 11 and 12) and shorter reaction time (Table 1, entry 13) diminished the yield of the product. Lower amount of 4-methoxybenzaldehyde will reduce the yield of the product (59%) (Table 1, entry 14).

With the optimized reaction conditions in hand, we then demonstrated the scope of this novel system for a variety of substrates. As shown in Table 2, a wide range of diaryl diselenides were smoothly coupled with aldehydes, giving the corresponding selenoesters in good to excellent yields. Diaryl diselenides bearing electron-donating and electron-withdrawing groups were successfully reacted with substituted aryl aldehydes. Remarkably, this system shows good functional group comparability, functional groups including bromo (Table 2, entries 1–5), trifluoromethyl (Table 2, entries 6–11), methoxy (Table 2, entries 16 and 17), amine (Table 2, entries 12 and 13)

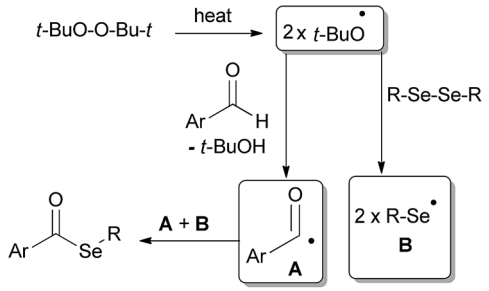
were all tolerated by the reaction conditions employed. Moreover, sterically demanding *ortho*-substituted aryl aldehydes underwent the C–Se bond formation with diselenides to provide the targets in good yields (Table 2, entry 2). Notably, heteroaromatic aldehydes such as thiophene-2-carboxaldehyde (Table 2, entries 5, 7, 14 and 16) and furan-containing aldehyde (Table 2, entries 8 and 17) are coupled with different diaryl diselenides bearing electron-donating and electron-withdrawing groups, provided the resulting selenoesters in good to excellent yields.

Table 3 DTBP-promoted coupling reaction of dialkyl diselenides with aldehydes[a]



Entry	Product		Yield[b] (%)
1		**4a**	91 (38)[c]
2		**4b**	84
3		**4c**	92
4		**4d**	67
5		**4e**	78
6		**4f**	69
7		**4g**	58
8		**4h**	51
9		**4i**	25

[a] Reaction conditions unless otherwise stated: aldehyde (1.0 mL), dialkyl diselenide (0.25 mmol) and DTBP (2.0 mmol) were reacted at 120 °C for 24 h using sealed tube. [b] Isolated yields based on diselenides. [c] Reactions were carried out using Schlenk tube.



Scheme 1 Plausible mechanism.

With the promising results in the coupling of aldehydes with diaryl diselenides, we next turned our attention to the use of dialkyl diselenides as the coupling partners in this system, the results are summarized in Table 3. A variety of aryl aldehydes bearing electron-withdrawing and electron-donating groups were successfully coupled with dialkyl diselenides, provided the corresponding selenoesters in moderate to excellent yields. Functional groups including chloro (Table 3, entry 8), trifluoromethyl (Table 3, entry 4), amine (Table 3, entries 1 and 2) were tolerated by the reaction conditions. Importantly, thiophene-containing alkyl selenoesters could also be formed in a 92% yield when the reaction was carried out by using 2-thiophenecarboxaldehyde as the coupling partner (Table 3, entry 3).

A potential mechanism for DTBP-promoted C–Se coupling reactions of aldehydes with diselenides is depicted in Scheme 1. The DTBP under heating can generate *t*-BuO radical which can react with aldehyde and diselenide to generate aldehydic radical **A** and selenide radical **B** respectively. The coupling of radical **A** and **B** can provide the selenoester.

Experimental section

General information

All chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer at the National Chung Hsing University.

General procedure for Table 1

A Schlenk tube equipped with a magnetic stirrer bar was charged with diphenyl diselenide (78.8 mg, 0.25 mmol), 4-methoxybenzaldehyde (1.0 mL) and oxidant (2.0 mmol) under a nitrogen-filled balloon and heated at 120 °C for 24 h in an oil bath. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to ambient temperature. The

resulting residue was purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3a**.

Se-phenyl 4-methoxybenzoselenoate (3a) (Table 1, entry 7).[17a] The title compound was prepared following the general procedure for Table 1, using diphenyl diselenide (78.8 mg, 0.25 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (2.0 mmol), which on purification by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1), provided **3a** as a white solid (135 mg, 93% yield). M.P.: 59–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.93 (dd, J = 2.0 & 6.8 Hz, 2H), 7.40 (dd, J = 2.0 & 4.8 Hz, 3H), 7.57–7.59 (m, 2H), 7.90 (dd, J = 2.0 & 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 114.0, 125.8, 128.8, 129.2, 129.5, 131.1, 136.3, 164.0, 191.2.

General procedure for Table 2

A Schlenk tube equipped with a magnetic stirrer bar was charged with diselenide (0.25 mmol), aldehyde (1.0 mL) and DTBP (2.0 mmol) under a nitrogen-filled balloon and heated at 120 °C for 24 h in an oil bath. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to ambient temperature. The resulting residue was purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3**.

Se-4-bromophenyl 3-methylbenzoselenoate (3b). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)diselane (118 mg, 0.25 mmol), 3-methylbenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3b** as a white solid (166 mg, 94% yield). M.P.: 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.39–7.41 (m, 3H), 7.50–7.52 (m, 2H), 7.69–7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 123.6, 124.5, 124.6, 127.6, 128.7, 132.3, 134.7, 137.7, 138.0, 138.8, 192.5; HRMS-EI calcd for $C_{14}H_{11}BrOSe$: 353.9158, found: 353.9162.

Se-4-bromophenyl 2-methylbenzoselenoate (3c). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)diselane (118 mg, 0.25 mmol), 2-methylbenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3c** as a white solid (156 mg, 88% yield). M.P.: 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 6H), 7.25 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.39–7.42 (m, 3H), 7.52–7.54 (m, 2H), 7.87 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 123.7, 125.7, 126.0, 128.8, 131.9, 132.42, 132.48, 136.6, 137.6, 137.8, 194.2; HRMS-EI calcd for $C_{14}H_{11}$-BrOSe: 353.9158, found: 353.9156.

Se-4-bromophenyl benzoselenoate (3d).[17b] The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)diselane (118 mg, 0.25 mmol), benzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **3d** as a white solid (129 mg, 76% yield). M.P.: 71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.63 (m, 7H), 7.89–7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8, 124.5, 127.3, 128.9, 132.4, 134.0, 137.7, 138.1, 192.5.

Se-4-bromophenyl 4-methoxybenzoselenoate (3e). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)diselane (118 mg, 0.25 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3e** as a white solid (115 mg, 62% yield). M.P.: 81–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.5, 114.1, 123.6, 124.7, 129.6, 130.8, 132.3, 137.8, 164.2, 190.4; HRMS-EI calcd for $C_{14}H_{11}BrO_2Se$: 369.9108, found: 369.9110.

Se-4-bromophenyl thiophene-2-carboselenoate (3f). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-bromophenyl)diselane (118 mg, 0.25 mmol), thiophene-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3f** as a white solid (152 mg, 88% yield). M.P.: 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, J = 0.8 & 4.0 Hz, 1H), 7.43–7.45 (m, 2H), 7.50–7.52 (m, 2H), 7.69 (dd, J = 1.2 & 4.8 Hz, 1H), 7.84 (dd, J = 1.2 & 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8, 124.2, 128.0, 132.1, 132.4, 133.9, 137.6, 142.5, 182.6; HRMS-EI calcd for $C_{11}H_7BrOSSe$: 345.8566, found: 345.8564.

Se-4-(trifluoromethyl)phenyl benzoselenoate (3g). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl)diselane (112 mg, 0.25 mmol), benzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3g** as a white solid (127 mg, 78% yield). M.P.: 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.50 (m, 2H), 7.60–7.72 (m, 5H), 7.90–7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.9 (d, J = 271.3 Hz), 125.9 (d, J = 3.7 Hz), 127.3, 129.0, 130.4, 131.0 (d, J = 32.8 Hz), 134.2, 136.4, 138.0, 192.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.2 (s); HRMS-EI calcd for $C_{14}H_9F_3OSe$: 329.9771, found: 329.9776.

Se-4-(trifluoromethyl)phenyl thiophene-2-carboselenoate (3h). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl) diselane (112 mg, 0.25 mmol), thiophene-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3h** as yellow solid (144 mg, 86% yield). M.P.: 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14–7.17 (m, 1H), 7.62–7.70 (m, 2H), 7.71–7.72 (m, 3H), 7.85–7.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8 (d, J = 270.3 Hz), 125.9 (d, J = 3.7 Hz), 128.1, 130.1, 131.0 (d, J = 32.8 Hz), 132.3, 134.1, 136.2, 142.4, 182.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.2 (s). HRMS-EI calcd for $C_{12}H_7F_3OSSe$: 335.9335, found: 335.9340.

Se-4-(trifluoromethyl)phenyl furan-2-carboselenoate (3i). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl)diselane (112 mg, 0.25 mmol), furan-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3i** as a yellow oil (118 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60 (dd, J = 1.6, 3.6 Hz, 1H), 7.23 (dd, J = 0.8, 3.6 Hz, 1H), 7.63–7.72 (m, 5H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 113.0, 115.7, 123.8 (d, J = 270.3 Hz), 125.9 (d, J = 3.7 Hz), 129.4, 131.0 (d, J = 32.8 Hz), 136.3, 146.9, 151.2, 179.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.2 (s); HRMS-EI calcd for $C_{12}H_7F_3O_2Se$: 319.9563, found: 319.9561.

Se-4-(trifluoromethyl)phenyl 4-chlorobenzoselenoate (3j). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl)diselane (112 mg, 0.25 mmol), 4-chlorobenzaldehyde (1.0 g) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **3j** as a white solid (140 mg, 77% yield). M.P.: 69–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J = 0.8, 8.4 Hz, 2H), 7.64–7.71 (m, 4H), 7.84 (dd, J = 0.8, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8 (d, J = 270.3 Hz), 125.9, 126.0 (d, J = 3.6 Hz), 128.6, 129.3, 130.0, 131.1 (d, J = 31.8 Hz), 136.3, 140.6, 190.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.2 (s). HRMS-EI calcd for $C_{14}H_8ClF_3OSe$: 363.9381, found: 363.9386.

Se-4-(trifluoromethyl)phenyl 4-methoxybenzoselenoate (3k). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl)diselane (112 mg, 0.25 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3k** as a white solid (106 mg, 59% yield). M.P.: 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.95 (dd, J = 2.0, 7.2 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.89 (dd, J = 2.0, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.2, 123.9 (d, J = 270.3 Hz), 125.8 (d, J = 3.6 Hz), 129.7, 130.6, 130.7, 131.0 (d, J = 23.7 Hz), 136.4, 164.4, 189.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.1 (s). HRMS-EI calcd for $C_{15}H_{11}F_3O_2Se$: 359.9876, found: 359.9872.

Se-4-(trifluoromethyl)phenyl 3-methylbenzoselenoate (3l). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-(trifluoromethyl)phenyl)diselane (112 mg, 0.25 mmol), 3-methylbenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **3l** as a white solid (89.2 mg, 52% yield). M.P.: 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.33–7.7.43 (m, 2H), 7.62–7.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 122.5, 123.9 (d, J = 270.3 Hz), 125.9 (d, J = 3.6 Hz), 127.7, 128.8, 130.6, 130.9 (d, J = 32.8 Hz), 134.9, 136.3, 138.0, 139.0, 191.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.2 (s); HRMS-EI calcd for $C_{15}H_{11}F_3OSe$: 343.9927, found: 343.9936.

Se-phenyl 4-(diethylamino)benzoselenoate (3m). The title compound was prepared following the general procedure for Table 2, using diphenyl diselenide (78.8 mg, 0.25 mmol), 4-(diethylamino)benzaldehyde (1.0 g) and DTBP (2.0 mmol), which on purification by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1), provided **3m** as a yellow solid (131 mg, 79% yield). M.P.: 104–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, J = 7.2 Hz, 6H), 3.30 (q, J = 7.2 Hz, 4H), 6.52 (d, J = 9.2 Hz, 2H), 7.28–7.29 (m, 2H), 7.50–7.52 (m, 3H), 7.71 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 44.5, 110.2, 124.8, 126.5, 128.4, 128.9, 130.0, 136.4, 151.8, 189.2; HRMS-EI calcd for $C_{17}H_{19}NOSe$: 333.0632, found: 333.0640.

Se-phenyl 4-(dimethylamino)benzoselenoate (3n). The title compound was prepared following the general procedure for Table 2, using diphenyl diselenide (78.8 mg, 0.25 mmol), 4-(dimethylamino)benzaldehyde (1.0 g) and DTBP (2.0 mmol), which on purification by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1), provided **3n** as a yellow solid (91 mg, 60% yield). M.P.: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (s, 6H), 6.55 (d, J = 9.2 Hz, 2H), 7.30–7.32 (m, 3H), 7.50–7.53 (m, 2H), 7.74 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.9, 110.7, 125.5, 126.4, 128.5, 129.0, 129.7, 136.4, 153.9, 189.7; HRMS-EI calcd for $C_{15}H_{15}NOSe$: 305.0319, found: 305.0310.

Se-phenyl thiophene-2-carboselenoate (3o).[17c] The title compound was prepared following the general procedure for Table 2, using diphenyl diselenide (78.8 mg, 0.25 mmol), thiophene-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), which on purification by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1), provided **3o** as a brown oil (86 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, J = 4.8 Hz, 1H), 7.39–7.41 (m, 3H), 7.58–7.60 (m, 2H), 7.67 (d, J = 5.2 Hz, 1H), 7.86 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.4, 127.9, 129.1, 129.3, 131.9, 133.16, 136.1, 142.9, 183.4.

Se-phenyl 3-methylbenzoselenoate (3p).[17c] The title compound was prepared following the general procedure for Table 2, using diphenyl diselenide (78.8 mg, 0.25 mmol), 3-methylbenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **3p** as a yellow oil (127 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 7.31–7.39 (m, 5H), 7.57–7.59 (m, 2H), 7.71–7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 124.5, 125.8, 127.6, 128.7, 128.9, 129.2, 134.5, 136.2, 138.4, 138.8, 193.3.

Se-4-methoxyphenyl thiophene-2-carboselenoate (3q). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-methoxyphenyl)diselane (93.0 mg, 0.25 mmol), thiophene-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3q** as a brown solid (131 mg, 88% yield). M.P.: 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 6.91–6.94 (m, 2H), 7.12–7.14 (m, 1H), 7.47–7.49 (m, 2H), 7.66 (dd, J = 1.2, 4.8 Hz, 1H), 7.85 (dd, J = 1.2, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 115.0, 115.7, 127.9, 131.8, 133.4, 137.7, 143.0, 160.4, 184.3; HRMS-EI calcd for $C_{12}H_{10}O_2SSe$: 297.9567, found: 297.9572.

Se-4-methoxyphenyl furan-2-carboselenoate (3r). The title compound was prepared following the general procedure for Table 2, using 1,2-bis(4-methoxyphenyl)diselane (93.0 mg, 0.25 mmol), furan-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **3r** as a brown solid (101 mg, 72% yield). M.P.: 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.56 (dd, J = 1.6, 3.6 Hz, 1H), 6.92–6.95 (m, 2H), 7.19 (d, J = 3.6 Hz, 1H), 7.47 (dd, J = 2.0, 6.8 Hz, 2H), 7.62 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.21, 112.7, 114.9, 115.0, 115.3, 137.8, 146.5, 151.7, 160.4, 181.6; HRMS-EI calcd for $C_{12}H_{10}O_3Se$: 281.9795, found: 281.9801.

General procedure for Table 3

A sealed tube equipped with a magnetic stirrer bar was charged with diselenide (0.25 mmol), aldehyde (1.0 mL) and DTBP (2.0 mmol) under a nitrogen-filled balloon and heated at 120 °C for

24 h in an oil bath. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to ambient temperature. The resulting residue was purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **4**.

Se-methyl 4-(diethylamino)benzoselenoate (4a). The title compound was prepared following the general procedure for Table 3, using dimethyl diselenide (0.024 mL, 0.25 mmol), 4-(diethylamino)benzaldehyde (1.0 g) and DTBP (2.0 mmol),-which on purification by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1), provided **4a** as a white solid (123 mg, 91% yield). M.P.: 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, J = 7.2 Hz, 6H), 2.31 (s, 3H), 3.38 (q, J = 7.2 Hz, 4H), 6.58 (d, J = 9.2 Hz, 2H), 7.78 (d, J = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.2, 12.3, 44.4, 110.1, 125.6, 129.6, 151.4, 191.0; HRMS-EI calcd for $C_{12}H_{17}NOSe$: 271.0475, found: 271.0472.

Se-methyl 4-(dimethylamino)benzoselenoate (4b). The title compound was prepared following the general procedure for Table 3, using dimethyl diselenide (0.024 mL, 0.25 mmol), 4-(dimethylamino)benzaldehyde (1.0 g) and DTBP (2.0 mmol),-which on purification by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1), provided **4b** as a white solid (102 mg, 84% yield). M.P.: 87–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.01 (s, 6H), 6.59 (d, J = 9.2 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.3, 39.9, 110.5, 126.4, 129.2, 153.7, 191.4; HRMS-EI calcd for $C_{10}H_{13}NOSe$: 243.0162, found: 243.0160.

Se-(*n*-heptyl) thiophene-2-carboselenoate (4c). The title compound was prepared following the general procedure for Table 3, using 1,2-diheptyldiselane (89.1 mg, 0.25 mmol), thiophene-2-carbaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **4c** as a colorless oil (133 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3H), 1.25–1.42 (m, 8H), 1.75 (t, J = 7.6 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H), 7.11 (dd, J = 4.0, 5.2 Hz, 1H), 7.63 (dd, J = 1.2, 4.8 Hz, 1H), 7.11 (dd, J = 1.2, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 26.0, 28.7, 29.8, 30.5, 31.6, 127.7, 131.3, 132.7, 144.2, 185.1; HRMS-EI calcd for $C_{12}H_{18}OSSe$: 290.0244, found: 290.0246.

Se-(*n*-heptyl) 4-(trifluoromethyl)benzoselenoate (4d). The title compound was prepared following the general procedure for Table 3, using 1,2-diheptyldiselane (89.1 mg, 0.25 mmol), 4-(trifluoromethyl)benzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **4d** as a colorless oil (118 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.4 Hz, 3H), 1.25–1.44 (m, 8H), 1.76 (t, J = 7.2 Hz, 2H), 3.13 (t, J = 7.2 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 26.3, 28.7, 29.9, 30.2, 31.6, 123.9 (d, J = 270.3 Hz), 125.8 (d, J = 3.7 Hz), 127.3, 134.6 (d, J = 32.8 Hz), 141.9, 194.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.7 (s); HRMS-EI calcd for $C_{15}H_{19}F_3OSe$: 352.0553, found: 352.0556.

Se-(*n*-heptyl) 4-*tert*-butylbenzoselenoate (4e). The title compound was prepared following the general procedure for Table 3, using 1,2-diheptyldiselane (89.1 mg, 0.25 mmol), 4-(*tert*-butyl)benzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **4e** as a yellow oil (132 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.26–1.43 (m, 17H), 1.71–1.76 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 25.5, 28.7, 29.6, 29.9, 30.5, 31.0, 31.7, 35.1, 125.6, 127.0, 136.6, 157.2, 194.3; HRMS-EI calcd for $C_{18}H_{28}OSe$: 340.1305, found: 340.1307.

Se-(*n*-heptyl) 3-methylbenzoselenoate (4f). The title compound was prepared following the general procedure for Table 3, using 1,2-diheptyldiselane (89.1 mg, 0.25 mmol), 3-methylbenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **4f** as a yellow oil (103 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3H), 1.25–1.43 (m, 8H), 1.70–1.76 (m, 2H), 2.39 (s, 3H), 3.07 (t, J = 7.2 Hz, 2H), 7.28–7.37 (m, 2H), 7.69–7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 21.1, 22.5, 25.6, 28.7, 29.6, 29.9, 30.4, 31.6, 124.3, 127.4, 128.5, 134.1, 138.5, 139.2, 195.0; HRMS-EI calcd for $C_{15}H_{22}OSe$: 298.0836, found: 298.0831.

Se-(*n*-heptyl) benzoselenoate (4g). The title compound was prepared following the general procedure for Table 3, using 1,2-diheptyldiselane (89.1 mg, 0.25 mmol), benzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **4g** as a colorless oil (82 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.25–1.43 (m, 8H), 1.71–1.76 (m, 2H), 3.09 (t, J = 7.6 Hz, 2H), 7.41–7.56 (m, 3H), 7.89–7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 25.7, 28.7, 29.9, 30.4, 31.6, 127.0, 128.6, 133.4, 139.2, 195.0; HRMS-EI calcd for $C_{14}H_{20}OSe$: 284.0679, found: 284.0672.

Se-(*n*-heptyl) 4-chlorobenzoselenoate (4h). The title compound was prepared following the general procedure for Table 3, using 1,2-diheptyldiselane (89.1 mg, 0.25 mmol), 4-chlorobenzaldehyde (1.0 g) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexane) to provide **4h** as a yellow oil (81.0 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86–0.89 (m, 3H), 1.28–1.42 (m, 8H), 1.72–1.76 (m, 2H), 3.07–3.11 (m, 2H), 7.39–7.42 (m, 2H), 7.82–7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 26.0, 28.7, 29.9, 30.3, 31.6, 128.3, 128.9, 137.5, 139.7, 193.7; HRMS-EI calcd for $C_{14}H_{19}ClOSe$: 318.0290, found: 318.0281.

Se-benzyl 4-methoxybenzoselenoate (4i). The title compound was prepared following the general procedure for Table 2, using 1,2-dibenzyldiselane (85.0 mg, 0.25 mmol), 4-methoxybenzaldehyde (1.0 mL) and DTBP (2.0 mmol), then purified by column chromatography (SiO_2, hexanes–EtOAc: 100 : 1) to provide **4i** as a yellow oil (38.2 mg, 25% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 4.32 (s, 2H), 6.90 (dd, J = 2.0, 6.8 Hz, 2H), 7.20–7.37 (m, 5H), 7.86 (dd, J = 2.0, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 55.5, 113.9, 126.8, 128.5, 128.9, 129.5, 131.6, 139.2, 164.0, 192.4; HRMS-EI calcd for $C_{15}H_{14}O_2Se$: 306.0159, found: 306.0153.

Conclusions

In conclusion, we have developed a general and efficient approach for the preparation of selenoesters using DTBP as an oxidant under metal-free and solvent-free conditions. This system shows good functional group compatibility, giving selenoesters in good to excellent yields.

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