A convenient alkoxylselenenylation of alkenes promoted by *p*-toluenesulfonic acid

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Abstract
In the presence of *p*-toluenesulfonic acid, the reaction of alkenes with diselenides and oxidant *m*-chloroperbenzoic acid proceeds efficiently in alcohols at room temperature, and was developed into a convenient procedure for the alkoxylselenenylation of alkenes, forming a series of corresponding 2-alkoxy-1-selenenyl compounds with high regioselectivity and good yields. The reaction conditions are optimized and a plausible mechanism for the acid promotion is suggested.

Keywords: Alkoxylselenenylation, diselenide, alkene, *p*-toluenesulfonic acid

Introduction

Organoselenium chemistry has developed rapidly over the past decades and selenium-based methodology has become a versatile tool in organic synthesis,[1-4] especially in synthesis of various important biological active and natural compounds.[5-7] The oxyselenenylation reaction is a useful procedure for the *anti*-l, 2-addition of an organoseleno group and an oxygen substituent (HO, RO, RCO_2) to an alkene.[8-10] In the electrophilic addition, the most common selenenylating reagents PhSeX (X = Cl, Br) are usually commercially available, but they can also be prepared by oxidative cleavage of diphenyl diselenide (PhSeSePh) by halogens.[11] However, the toxic and moisture-sensitive nature of PhSeX, and the nucleophilic halide anions are sometimes responsible for undesirable processes such as addition of the halide ion and a decrease in stereoselectivity. Some alternative methods have been developed such as the oxidative cleavage of PhSeSePh with ammonium peroxydisulfate,[8-9,12] *m*-nitrobenzenesulfonyl peroxide,[13-14] 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[15] and *N*-phenylselenosaccharin (NPSSac).[16] Cupric catalytic oxidation[17-18] and electrolytic oxidation[19-21] are other efficient methods. Using hypervalent iodine reagents can mediate the oxidative cleavage of PhSeSePh, and the electrophilic addition of the *in situ* generated reactive electrophilic selenium species to alkenes proceeds smoothly.[22-29] However, in the above methods some oxidants are toxic or expensive,

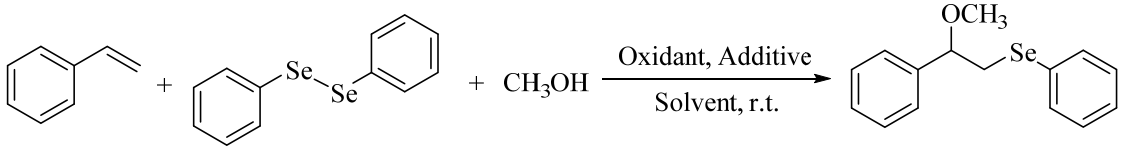
some oxidations need long reaction time or high reaction temperature, which limits their applicability.

Recently, we have investigated the novel catalytic oxyselenenylation of alkenes, and found that acidic additives can promote the oxyselenenylation. Herein, we report a novel and convenient alkoxylselenenylation of alkenes with PhSeSePh in the presence of *p*-toluenesulfonic acid (TsOH) and an easily available oxidant, *m*-chloroperbenzoic acid (*m*CPBA). Using the novel method, a series of corresponding 2-alkoxyl-1-selenenylation compounds, mostly new compounds, were prepared with high regioselectivity and good yields.

Results and Discussion

We first examined the reaction of PhSeSePh with 1.5 equiv. of styrene and 0.6 equiv. of oxidant H_2O_2 in methanol at room temperature, and found that the desired product 2-methoxy-2-phenylethyl phenyl selenide was obtained in only 5% yield after 12 hours (Table 1, entry 1). When 1.0 equiv. of TsOH was added to the reaction mixture, the yield increased greatly up to 78% (entry 2), meaning that TsOH promotes the alkoxylselenenylation of alkenes. The reaction conditions were optimized and the results are summarized in Table 1. Compared with methanol, several mixture solvents were not suitable for the reaction, giving poor or low yields (entries 3-7). Other acidic additives were tested, and the results revealed that they can mediate the reaction, but the observed yields were not more than 78% (entries 8-12). Several oxidants were used in place of H_2O_2, but *m*CPBA proved to be the most effective (entries 2, 13-16). Although oxygen in air was also effective for the reaction, a long reaction time was needed (entry 17). In the absence of oxidant, no product was observed (entry 18). The amounts of TsOH and *m*CPBA were checked: 1.0 equiv. of TsOH and 0.6 equiv. of *m*CPBA were suitable for the reaction (entries 13, 19-25). As shown in Table 1, the optimal amount of styrene was 1.5 equiv. and a suitable reaction time was 6 hours (entries 13, 26-30).

Table 1. Optimization of TsOH-promoted alkoxylselenenylation of alkenes



Entry	Styrene (equiv.)	Oxidant (equiv.)	Additive (equiv.)	Solvent	Time (h)	Yield (%)[a]
1	1.5	H_2O_2 (0.6)	---	CH_3OH	12	5
2	1.5	H_2O_2 (0.6)	TsOH (1.0)	CH_3OH	12	78
3	1.5	H_2O_2 (0.6)	TsOH (1.0)	CH_3OH-CH_2Cl_2 (1:1)	12	45
4	1.5	H2O2 (0.6)	TsOH (1.0)	CH3OH-CH3CN (1:1)	12	62

Table 1. Continued

Entry	Styrene (equiv.)	Oxidant (equiv.)	Additive (equiv.)	Solvent	Time (h)	Yield (%)[a]
5	1.5	H_2O_2 (0.6)	TsOH (1.0)	CH_3OH-H_2O (1:1)	12	48
6	1.5	H_2O_2 (0.6)	TsOH (1.0)	CH_3OH-Et_2O (1:1)	12	39
7	1.5	H_2O_2 (0.6)	TsOH (1.0)	CH_3OH-EtOAc (1:1)	12	52
8	1.5	H_2O_2 (0.6)	HCl (1.0)	CH_3OH	12	49
9	1.5	H_2O_2 (0.6)	CF_3CO_2H (1.0)	CH_3OH	12	17
10	1.5	H_2O_2 (0.6)	$AlCl_3$ (1.0)	CH_3OH	12	47
11	1.5	H_2O_2 (0.6)	$FeCl_3$ (1.0)	CH_3OH	12	77
12	1.5	H_2O_2 (0.6)	$BF_3.Et_2O$ (1.0)	CH_3OH	12	75
13	1.5	*m*CPBA (0.6)	TsOH (1.0)	CH_3OH	12	84
14	1.5	$NaBO_3.H_2O$ (0.6)	TsOH (1.0)	CH_3OH	12	70
15	1.5	TBHP (0.6)	TsOH (1.0)	CH_3OH	12	53
16	1.5	Oxone (0.6)	TsOH (1.0)	CH_3OH	12	32
17	1.5	---[b]	TsOH (1.0)	CH_3OH	72	70
18	1.5	---[c]	TsOH (1.0)	CH_3OH	72	0
19	1.5	*m*CPBA (0.6)	---	CH_3OH	12	6
20	1.5	*m*CPBA (0.6)	TsOH (0.5)	CH_3OH	12	55
21	1.5	*m*CPBA (0.6)	TsOH (0.75)	CH_3OH	12	67
22	1.5	*m*CPBA (0.6)	TsOH (1.25)	CH_3OH	12	80
23	1.5	*m*CPBA (0.5)	TsOH (1.0)	CH_3OH	12	82
24	1.5	*m*CPBA (0.75)	TsOH (1.0)	CH_3OH	12	76
25	1.5	*m*CPBA (1.0)	TsOH (1.0)	CH_3OH	12	70
26	1.2	*m*CPBA (0.6)	TsOH (1.0)	CH3OH	12	78
27	2.0	*m*CPBA (0.6)	TsOH (1.0)	CH_3OH	12	83
28	1.5	*m*CPBA (0.6)	TsOH (1.0)	CH_3OH	2	71
29	1.5	*m*CPBA (0.6)	TsOH (1.0)	CH_3OH	4	79
30	1.5	*m*CPBA (0.6)	TsOH (1.0)	CH_3OH	6	85

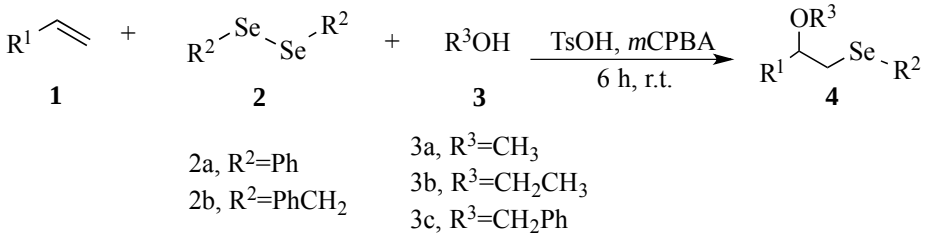
[a] Isolated Yield.

[b] The reaction was carried out in air without *m*CPBA.

[c] The reaction was carried out in N_2 without *m*CPBA.

Using the optimum reaction conditions, we investigated the TsOH promoted alkoxylselenenylation of 1.5 equiv. of alkenes (1), 1.0 equiv. diselenides (2) and 0.6 equiv. of

*m*CPBA in the presence of 1.0 equiv. of TsOH in alcohol at room temperature for 6 hours (Scheme 1) and the results are summarized in Table 2.



Scheme 1. TsOH-promoted alkoxylselenenylation of alkenes.

Table 2. TsOH-promoted alkoxylselenenylation of alkenes

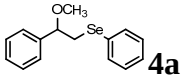
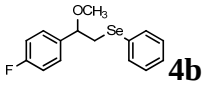
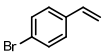
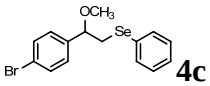
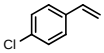
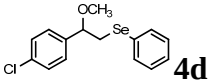
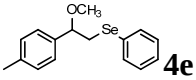
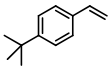
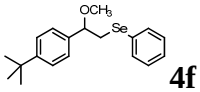
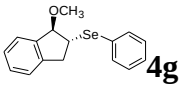
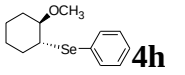
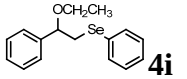
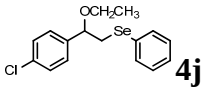
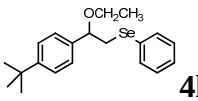
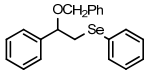
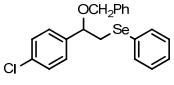
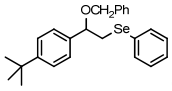
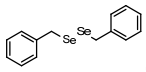
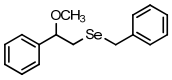
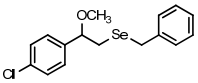
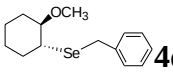
Entry	Alkene	Diselenide	Alcohol	Product	Yield(%)[a]
1	 **1a**	PhSeSePh **2a**	CH_3OH **3a**	 **4a**	85
2	 **1b**	**2a**	**3a**	 **4b**	77
3	 **1c**	**2a**	**3a**	 **4c**	86
4	 **1d**	**2a**	**3a**	 **4d**	90
5	 **1e**	**2a**	**3a**	 **4e**	75
6	 **1f**	**2a**	**3a**	 **4f**	81
7	 **1g**	**2a**	**3a**	 **4g**	92
8	 **1h**	**2a**	**3a**	 **4h**	82
9	**1a**	**2a**	CH_3CH_2 OH **3b**	 **4i**	64
10	**1d**	**2a**	**3b**	 **4j**	61

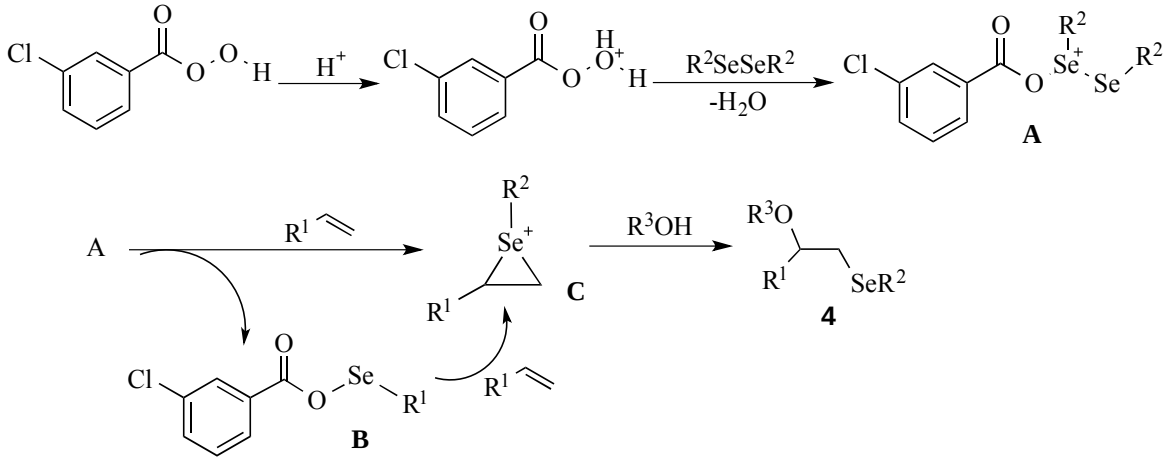
Table 2. Continued

Entry	Alkene	Diselenide	Alcohol	Product	Yield(%)[a]
11	**1f**	**2a**	**3b**	 **4k**	50
12	**1a**	**2a**	$PhCH_2O$ H **3c**	 **4l**	60
13	**1d**	**2a**	**3c**	 **4m**	75
14	**1f**	**2a**	**3c**	 **4n**	45
15	**1a**	 **2b**	**3a**	 **4o**	72
16	**1d**	**2b**	**3a**	 **4p**	78
17	**1h**	**2b**	**3a**	 **4q**	74

[a] Isolate yields.

As can be seen from Table 2, the reaction was compatible with most of the studied alkenes and the corresponding 2-methoxy-1-selenenylation compounds were obtained in good to excellent yields (Table 2, entries 1-6). Cyclic alkenes **1g** and **1h** under the same conditions gave *trans* adducts with excellent yields (entries 7 and 8). When the reaction was carried out in ethanol or benzyl alcohol, the yields for the corresponding products were somewhat lower than those in methanol (entries 9-14). Dibenzyl diselenide (**2b**), also reacted easily with alkenes, but the yields were slightly lower (entries 15-17).

A plausible reaction pathway is shown in Scheme 2. Thus, in the presence of TsOH, *m*CPBA becomes more electrophilic by elimination of H_2O, which reacts with diselenide to form the active intermediate **A**,[13] followed by a rapid cleavage of the Se-Se bond and the electrophilic selenium species produced then reacts with alkene to produce an unstable cyclic intermediate **C**.[18] The *in situ* generated another active intermediate **B** can further transfer a second equivalent of electrophilic selenium to alkenes to form the cyclic intermediate **C**. After solvolysis of **C** in alcohol, the desired product *anti*-2-alkoxy-1-selenenylation compound **4** as a single isomer is obtained.[20]



Scheme 2. Proposed mechanism for TsOH-promoted alkoxylselenenylation of alkenes.

Conclusions

We have developed a new and convenient strategy for the synthesis of 2-alkoxy-1-selenenylation compounds by the electrophilic addition of alkenes with diselenides and *m*CPBA in the presence of TsOH at room temperature. This method has some advantages such as mild reaction conditions and a simple procedure, which provided a series of 2-alkoxy-1-selenenylation compounds, mostly new compounds with high regioselectivity and good yields. Other acidic additives that promot convenient *anti*-l, 2-addition of an organylseleno group and an oxygen substituent to unsaturated functions will be reported in due course.

Experimental Section

General. IR spectra were recorded on a Thermo-Nicolet 6700 instrument, ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker-AVANCE Ⅲ (500 MHz) spectrometer, mass spectra were determined on Waters-GCT Premier, Thermo-DECAX-60000 LCQ Deca XP and Thermo-ITQ 1100 mass spectrometers. Alkenes, diselenides, *m*CPBA, TsOH, MeOH, EtOH and benzyl alcohol were commercially available.

General procedure for TsOH-promoted alkoxylselenenylation of alkenes. To methanol (1 mL), styrene (0.3 mmol), PhSeSePh (0.1 mmol) and TsOH (0.2 mmol) were respectively added, after then *m*CPBA (0.12 mmol) was added. The mixture was vigorously stirred at room temperature for 6 h. Upon completion, saturated aqueous $Na_2S_2O_3$ (2 mL), saturated aq Na_2CO_3 (8 mL) and H_2O (5 mL) were successively added to the mixture, and the mixture was vigorously stirred for another 5 min. The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic layers was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced

pressure. The residue was purified on a silica gel plate (4:1 petroleum ether-EtOAc) to give 2-methoxy-2-phenylethyl phenyl selenide **4a** in 85% yield.

2-Methoxy-2-phenylethyl phenyl selenide (4a).[30] Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.40-7.29 (m, 5H), 7.40-7.29 (m, 5H), 7.28-7.22 (m, 3H), 4.37 (dd, 8.4, 5.0 Hz, 1H), 3.34 (dd, 12.3, 8.5 Hz, 1H), 3.27 (s, 3H), 3.12 (dd, 12.3, 5.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.0, 132.6, 130.7, 129.0, 128.5, 128.1, 126.8, 126.7, 83.3, 57.0, 35.4; IR (ν_{max}, cm^{-1}): 3059.2, 2932.4, 2821.5, 1579.0, 1477.6, 1106.0, 736.2, 701.9; MS (EI, *m/z*,%): 292 (M^+, 3.4), 122 (100).

(2-(4-Fluorophenyl)-2-methoxyethyl phenyl selenide (4b). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.30-7.24 (m, 5H), 7.07-7.01 (m, 2H), 4.35 (dd, 8.0, 5.5 Hz, 1H), 3.32 (dd, 12.3, 8.0 Hz, 1H), 3.25 (s, 3H), 3.09 (dd, 12.3, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 161.5, 136.6 (d, 2.5 Hz), 132.7, 130.5, 129.7, 129.0, 128.4 (d, 7.5 Hz), 126.9, 115.4 (d, 21.3 Hz), 82.6, 56.9 , 35.3; IR ($\nu_{max,}$ cm^{-1}): 3070.6, 2932.8, 1728.1, 1508.4, 1224.7, 1105.9, 836.8, 737.1; MS (EI, *m/z*, %): 310 (M^+, 3.0), 140 (100); HRMS calcd for [M^+] ($C_{15}H_{15}FOSe$), 310.0272; found 310.0253.

(2-(4-Bromophenyl)-2-methoxyethyl phenyl selenide (4c). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.45 (m, 4H), 7.28-7.24 (m, 3H), 7.20-7.17 (m, 2H), 4.32 (dd, 7.9, 5.5 Hz, 1H), 3.30 (dd, 12.4, 7.9 Hz, 1H), 3.25 (s, 3H), 3.08 (dd, 12.4, 5.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 132.8, 131.7, 130.4, 129.1, 128.5, 127.0, 122.0, 82.7, 57.1, 35.1; IR ($\nu_{max,}$ cm^{-1}): 2931.1, 2821.2, 1727.6, 1578.5, 1478.7, 1259.5, 1101.2, 822.5, 737.0, 691.1; MS (EI, *m/z*,%): 370 (M^+, 4.6), 202 (100); HRMS calcd for [M^+] ($C_{15}H_{15}BrOSe$), 369.9471; found 369.9457.

(2-(4-Chlorophenyl)-2-methoxyethyl phenyl selenide (4d). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.33-7.31 (m, 2H), 7.28-7.24 (m, 5H), 4.33 (dd, 7.9, 5.5 Hz, 1H), 3.30 (dd, *J* = 12.4, 8.0 Hz, 1H), 3.25 (s, 3H), 3.08 (dd, 12.4, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 133.8, 132.7, 130.4, 129.0, 128.7, 128.1, 126.9, 82.6, 57.0, 35.1;
IR ($\nu_{max,}$ cm^{-1}): 2931.9, 2921.8, 1727.9, 1477.9, 1087.7, 826.7, 736.9, 691.1; MS (EI, *m/z*, %): 326 (M^+, 4.3), 156 (100); HRMS calcd for [M^+] ($C_{15}H_{15}ClOSe$), 325.9977; found 325.9947.

2-Methoxy-2-(*p*-tolyl)ethyl phenyl selenide (4e) Colorless viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.28-7.17 (m, 7H), 4.34 (dd, 8.4, 5.1 Hz, 1H), 3.35 (dd, 12.2, 8.4 Hz, 1H), 3.26 (s, 3H), 3.12 (dd, 12.2, 5.1 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.8, 132.5, 130.8, 129.2, 129.0, 126.7, 126.6, 83.0, 56.9, 35.4, 21.2; IR ($\nu_{max,}$ cm^{-1}): 2930.7, 2820.3, 1728.8, 1578.9, 1477.6, 1102.8, 736.3; MS (EI, *m/z*, %): 306 (M^+, 3.1), 135 (100); HRMS calcd for [M^+] ($C_{16}H_{18}OSe$), 306.0523; found 306.0521.

2-(4-*t*-Butyl)phenyl)-2-methoxyethyl phenyl selenide (4f). Pale yellow viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.39-7.37 (m, 2H), 7.28-7.23 (m, 5H), 4.37 (dd, 8.5, 4.9 Hz, 1H), 3.35 (dd, 12.3, 8.5 Hz, 1H), 3.27 (s, 3H), 3.13 (dd, 12.3, 4.9 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 137.8, 132.6, 130.9, 129.0, 126.7, 126.4, 125.4, 83.1, 57.0, 35.4, 34.6, 31.4; IR ($\nu_{max,}$ cm^{-1}): 3056.2, 2962.5, 2820.8, 1477.4, 1105.4, 831.7, 735.9, 691.1; MS (EI, *m/z*,%): 348 (M^+, 1.5), 177 (100); HRMS calcd for [M^+] ($C_{19}H_{24}OSe$), 348.0992; found

348.0981.

1-Methoxy-2-indanyl phenyl selenide (4g).[20] Pale yellow viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.60 (m, 2H), 7.42 (d, 7.2 Hz, 1H), 7.34-7.29 (m, 4H), 7.28-7.23 (m, 2H), 4.79 (d, 2.9 Hz, 1H), 4.05 (dt, 7.0, 3.4 Hz, 1H), 3.62 (dd, 17.0, 7.4 Hz, 1H), 3.39 (s, 3H), 2.97 (dd, 17.0, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.9, 134.3, 129.6, 129.2, 129.0, 127.6, 126.9, 125.6, 125.0, 90.1, 56.9, 44.7, 38.4; IR ($\nu_{max,}$ cm^{-1}): 3070.7, 2926.6, 2819.9, 1578.6, 1477.5, 1082.3, 738.5, 691.9; MS (EI, *m/z*,%): 304 (M^+, 9.4), 147 (100).

2-Methoxycyclohexyl phenyl selenide (4h).[31] Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.29-7.25 (m, 3H), 3.39 (s, 3H), 3.30-3.25 (m, 1H), 3.21-3.16 (m, 1H), 2.19-2.13 (m, 1H), 2.04-1.98 (m, 1H), 1.78-1.69 (m, 1H), 1.65-1.57 (m, 1H), 1.53-1.49 (m, 1H), 1.34-1.22 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.3, 132.9, 128.8, 127.4, 82.2, 77.3, 77.0, 76.8, 56.4, 47.4, 32.1, 30.3, 25.7, 23.4; IR ($\nu_{max,}$ cm^{-1}): 2932.0, 2856.1, 1729.9, 1436.9, 1189.2, 739.8, 692.7; MS (EI, *m/z*, %): 270 (M^+, 10.5), 81 (100).

2-Ethoxy-2-phenylethyl phenyl selenide (4i).[30] Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.39-7.28 (m, 5H), 7.28-7.23 (m, 3H), 4.49 (dd, 8.4, 5.1 Hz, 1H), 3.46-3.33 (m, 3H), 3.12 (dd, 12.2, 5.1 Hz, 1H), 1.20 (t, 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 132.6, 130.9, 129.0, 128.5, 127.9, 126.7, 126.6, 81.5, 64.7, 35.6, 15.2; IR ($\nu_{max,}$ cm^{-1}): 2973.6, 2863.3, 1579.1, 1477.7, 1091.6, 735.9, 701.7; MS (EI, *m/z*,%): 306 (M^+, 6.4), 135 (100).

2-(4-Chlorophenyl)-2-ethoxyethyl phenyl selenide (4j). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.32-7.30 (m, 2H), 7.28-7.23 (m, 5H), 4.45 (dd, *J* = 8.0, 5.5 Hz, 1H), 3.42-3.36 (m, 2H), 3.34-3.29 (m, 1H), 3.07 (dd, 12.3, 5.5 Hz, 1H), 1.19 (t, 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 133.6, 132.7, 130.6, 129.0, 128.6, 128.0, 126.9, 80.8, 64.8, 35.3, 15.2; IR ($\nu_{max,}$ cm^{-1}): 2974.6, 2869.3, 1578.8, 1478.1, 1088.8, 826.4, 736.2; MS (EI, *m/z*,%): 340 (M^+, 4.3), 169 (100); HRMS calcd for [M^+] ($C_{16}H_{17}ClOSe$), 340.0134; found 340.0103.

2-(4-*t*-Butyl)phenyl)-2-ethoxyethyl phenyl selenide (4k). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.38-7.35 (m, 2H), 7.28-7.21 (m, 5H), 4.48 (dd, 8.6, 5.0 Hz, 1H), 3.44 (dq, 9.2, 7.0 Hz, 1H), 3.41-3.32 (m, 2H), 3.11 (dd, 12.2, 5.0 Hz, 1H), 1.33 (s, 9H), 1.20 (t, 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 138.6, 132.5, 131.1, 128.9, 126.6, 126.3, 125.3, 64.6, 35.6, 34.5, 31.4, 15.2; IR ($\nu_{max,}$ cm^{-1}): 2964.8, 2867.6, 1579.2, 1477.4, 1091.9, 735.6; MS (EI, *m/z*, %): 362 (M^+, 1.9), 191 (100); HRMS calcd for [M^+] ($C_{20}H_{26}OSe$), 362.1149; found 362.1141.

2-Benzyloxy-2-phenylethyl phenyl selenide (4l). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.44-7.29 (m, 10H), 7.28-7.23 (m, 3H), 4.62 (dd, 8.5, 5.1 Hz, 1H), 4.53 (d, 11.8 Hz, 1H), 4.35 (d, 11.8 Hz, 1H), 3.44 (dd, 12.4, 8.5 Hz, 1H), 3.20-3.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 138.1, 132.5, 130.8, 129.0, 128.6, 128.3, 128.2, 127.8, 127.6, 126.8, 126.7, 80.8, 70.8, 35.5; IR ($\nu_{max,}$ cm^{-1}): 3061.1, 3029.6, 2864.7, 1578.8, 1453.3, 1092.3, 735.2, 699.8; MS (EI, *m/z*,%): 368 (M^+, 6.7), 197 (100); HRMS calcd for [M^+] ($C_{21}H_{20}OSe$), 368.0679; found 368.0665.

2-Benzyloxy-2-(4-chlorophenyl)ethyl phenyl selenide (4m). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.41 (m, 2H), 7.39-7.27 (m, 9H), 7.25-7.22 (m, 3H), 4.56 (dd, 7.9, 5.6

Hz, 1H), 4.49 (d, 11.8 Hz, 1H), 4.32 (d, 11.8 Hz, 1H), 3.39 (dd, 12.4, 7.9 Hz, 1H), 3.12 (dd, 12.4, 5.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 137.8, 133.8, 132.6, 130.5, 129.0, 128.8, 128.4, 128.2, 127.8, 127.7, 126.8, 80.1, 70.9, 35.2; IR ($\nu_{max,}$ cm^{-1}): 3061.8, 2864.4, 1723.7, 1490.5, 1088.3, 827.4, 735.7; MS (EI, *m/z*,%): 402 (M^+, 1.9), 92 (100); HRMS calcd for [M^+] ($C_{21}H_{19}ClOSe$), 402.0290; found 402.0277.

2-Benzyloxy-2-(4-*t*-butyl)phenylethyl phenyl selenide (4n). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.41-7.39 (m, 2H), 7.36-7.32 (m, 4H), 7.31-7.27 (m, 3H), 7.23-7.21 (m, 3H), 4.59 (dd, 8.5, 5.0 Hz, 1H), 4.53 (d, 11.8 Hz, 1H), 4.33 (d, 11.8 Hz, 1H), 3.42 (dd, 12.3, 8.6 Hz, 1H), 3.15 (dd, 12.3, 4.9 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 138.2, 138.0, 132.5, 131.0, 128.9, 128.3, 127.8, 127.5, 126.6, 126.5, 125.5, 80.6, 70.8, 35.6, 34.6, 31.4; IR ($\nu_{max,}$ cm^{-1}): 3058.9, 2962.3, 2866.3, 1579.0, 1477.2, 1093.0, 833.9, 734.8; MS (EI, *m/z*,%): 424 (M^+, 1.9), 161 (100); HRMS calcd for [M^+] ($C_{25}H_{28}OSe$), 424.1305; found 424.1288.

Benzyl 2-methoxy-2-phenylethyl selenide (4o).[30] Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.34-7.32 (m, 1H), 7.31-7.26 (m, 6H), 7.24-7.20 (m, 1H), 4.22 (dd, 8.0, 5.4 Hz, 1H), 3.75-3.68 (m, 2H), 3.24 (s, 3H), 2.92 (dd, *J* = 12.7, 8.0 Hz, 1H), 2.69 (dd, 12.7, 5.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 139.5, 129.0, 128.5, 128.4, 128.0, 126.7, 126.7, 84.3, 56.9, 30.9, 27.9; IR ($\nu_{max,}$ cm^{-1}):2928.3, 2820.8, 1725.7, 1493.2, 1105.2, 1105.2, 757.7, 698.5; MS (EI, *m/z*,%): 306 (M^+, 7.7), 91 (100).

Benzyl 2-(4-chlorophenyl)-2-methoxyethyl selenide (4p). Colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.31-7.25 (m, 4H), 7.25-7.19 (m, 3H), 4.17 (dd, 7.7, 5.5 Hz, 1H), 3.74 (dd, 15.5, 11.9 Hz, 2H), 3.22 (s, 3H), 2.87 (dd, 12.8, 7.8 Hz, 1H), 2.64 (dd, *J* = 12.7, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 139.3, 133.7, 129.0, 128.7, 128.5, 128.1, 126.7, 83.6, 56.9, 30.7, 28.0; IR ($\nu_{max,}$ cm^{-1}): 2928.6, 2821.1, 1598.2, 1491.8, 1088.1, 826.9, 697.6; MS (EI, *m/z*,%): 340 (M^+, 1.4), 156 (100); HRMS calcd for [M^+] ($C_{16}H_{17}ClOSe$), 340.0133; found 340.0121.

Benzyl 2-methoxycyclohexyl selenide (4q).[32] Pale yellow viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 3.98-3.90 (m, 2H), 3.37 (s, 3H), 3.19-3.17 (m, 1H), 2.95-2.91 (m, 1H), 2.10-2.08 (m, 2H), 1.72-1.71 (m, 1H), 1.63-1.61 (m, 1H), 1.52-1.44 (m, 1H), 1.33-1.27 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 129.0, 128.4, 126.5, 83.8, 56.4, 43.3, 31.5, 30.3, 27.6, 25.6, 23.3; IR ($\nu_{max,}$ cm^{-1}): 29930.9, 2855.4, 1493.8, 1110.2, 1088.4, 758.0, 296.9; MS (EI, *m/z*,%): 284 (M^+, 3.9), 155 (100).

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