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Stereoselective *Z*-iodoalkoxylation of 1,2-allenyl sulfides or selenides

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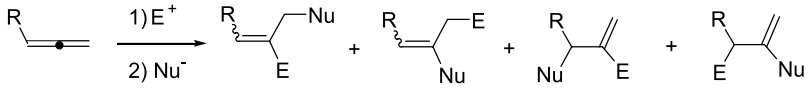
Abstract—Iodoalkylation of 1,2-allenyl sulfides or selenides with I_2 in MeCN/ROH (20:1) afforded *Z*-3-alkoxy-2-iodopropenyl sulfides or selenides in high stereoselectivity and moderate to good yields. The carbon–iodine bonds in these compounds may undergo Suzuki, Negishi, and Sonogashira coupling reaction smoothly.

1. Introduction

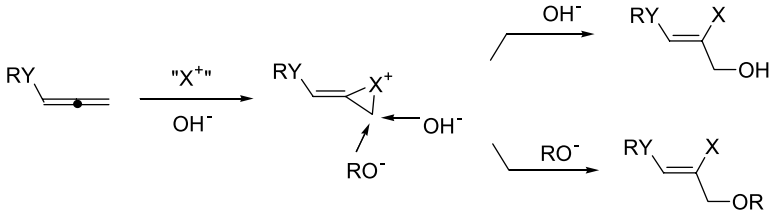
Electrophilic addition of allenes is an interesting reaction since usually two different functionalities can be introduced within one operation. However, the regio- and stereoselectivity is usually low, which makes these reactions synthetically unattractive (Scheme 1).[1]

Recently, we have applied the strategy of introducing heteroatoms into allenes to control the regio- and stereoselectivity of the halohydroxylation of allenes.[2–4] With 1,2-allenyl sulfoxides, *E*-halohydroxylation was realized by the participation of the sulfinyl oxygen[2] while the *Z*-halohydroxylation of 1-sulfur or selenium-substituted allene was probably controlled by the Lewis acid–base interaction between X^+ and sulfur or selenium atom.[3–5]

Based on the *Z*-halohydroxylation results of 1,2-allenyl sulfides and selenides, we reasoned that if the reaction is conducted in the presence of a nucleophile[6] other than water, the nucleophile can be introduced instead of the hydroxyl group (Scheme 2). In this paper, we wish to report our recent observation of using alcohols as the nucleophile.[7]



Scheme 1.



Scheme 2.

Keywords: Iodoalkoxylation; Allenes; Sulfides; Selenides; Coupling.
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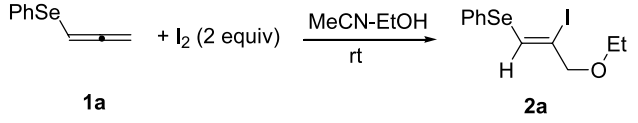
Table 1. Iodoethoxylation reaction of **1a** under different conditions[a]

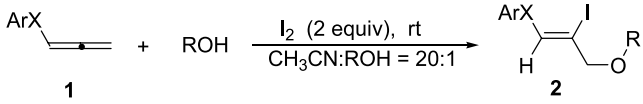


1a **2a**

Entry	CH_3CN/EtOH	Time (h)	Yield (%)[b]
1	1:1	1.5	59
2	4:1	1.5	50
3	9:1	1	55
4	27:1	1.5	17
5	20:1	1	68
6[c]	20:1	2.5	48
7[d]	20:1	1	45
8[e]	20:1	1	54
9[f]	20:1	1	54

[a] The reaction was conducted using 0.25 mmol of **1a**, 0.5 mmol of I_2 and EtOH (0.25 mL).
[b] Isolated yield.
[c] The reaction was conducted at 0 °C.
[d] The reaction was conducted at 30 °C.
[e] 1.5 equiv of I_2 were used.
[f] 3 equiv of I_2 were applied.

Table 2. Reaction of **1** with different alcohols[a]



1 **2**

Entry	Ar	X	ROH	Yield (%)[b]
1	Ph	Se	EtOH	68 (**2a**)
2	Ph	Se	*i*-Butanol	63 (**2b**)
3	Ph	Se	Pentanol	76 (**2c**)
4	Ph	Se	Cyclohexanol	80 (**2d**)
5	Ph	Se	BnOH	77 (**2e**)
6	Bn	Se	EtOH	64 (**2f**)
7	Ph	S	EtOH	49 (**2g**)

[a] The reaction was conducted with substrate I_2 (2 equiv) and CH_3CN/ROH 20:1 at room temperature for 1 h.
[b] Isolated yield.

2. Results and discussion

We tried the reaction of 1,2-propdienyl phenyl selenide with EtOH and I_2. In the presence of 2 equiv of I_2, the effect of the ratio of MeCN/EtOH on the reaction was studied (entries 1–5, Table 1). Best result was obtained with a ratio of MeCN/EtOH of 20:1 to afford **2a** in 68% yield (entry 5, Table 1).

The reaction at a lower or higher temperature afforded the product **2a** in relatively lower yields (entries 6 and 7, Table 1). With 1.5 or 3 equiv of I_2, the yields of **2a** were also lower (54%) (entries 8 and 9, Table 1).

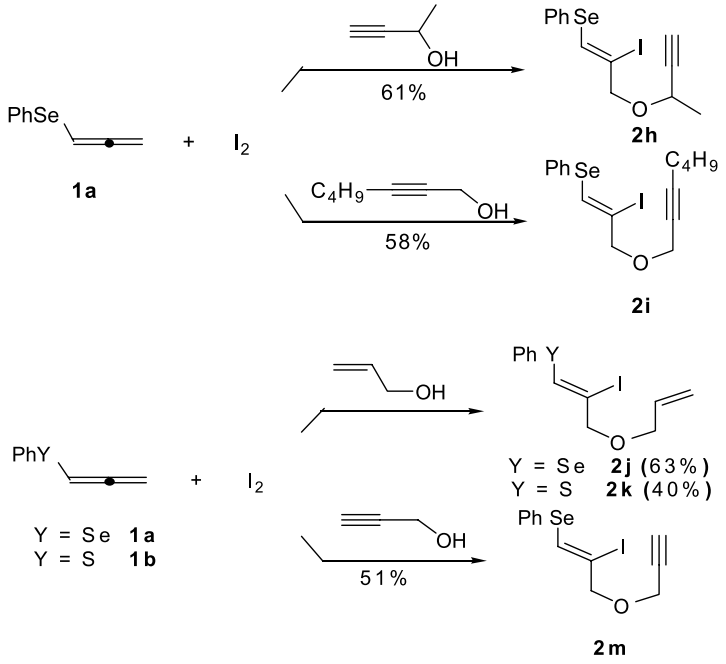
With the standard reaction conditions in hand, we studied the effect of the structure of alcohols on the reaction with some of the typical examples listed in Table 2. In all these cases, the reaction afforded the products, that is, 2(*Z*)-iodoallylic ethers **2a–g** highly stereoselectively in moderate to good yields.

Furthermore, it is interesting to observe that allyl alcohol and propargyl alcohol can also react similarly affording the corresponding allylic or proparylic ethers **2h–2m** in reasonable yields (Scheme 3).

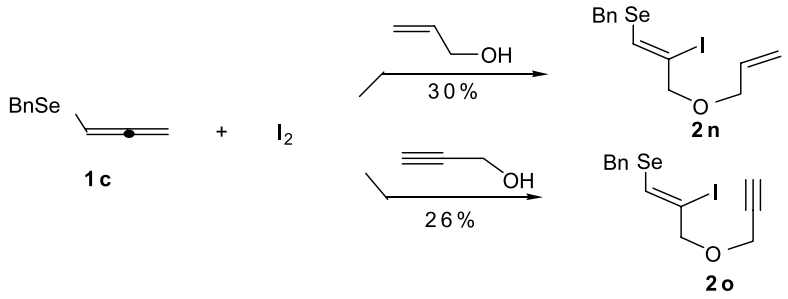
However, the reaction of the corresponding benzyl selenide afforded products in much lower yields (Scheme 4).

The stereoselectivity, which was determined by the NOE study of **2a**, is similar to what was observed with the halohydroxylation,[3,4] affording the *Z*-isomers highly stereoselectively.

The carbon–iodine bond in **2a** can undergo Suzuki coupling[8] (Table 3), Sonogashira coupling reaction[9] and Negishi coupling[10] (Scheme 5) to afford the stereodefined allylic ethers **3aa–3af**.

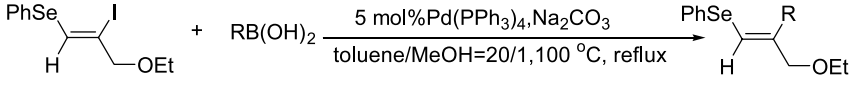


Scheme 3.

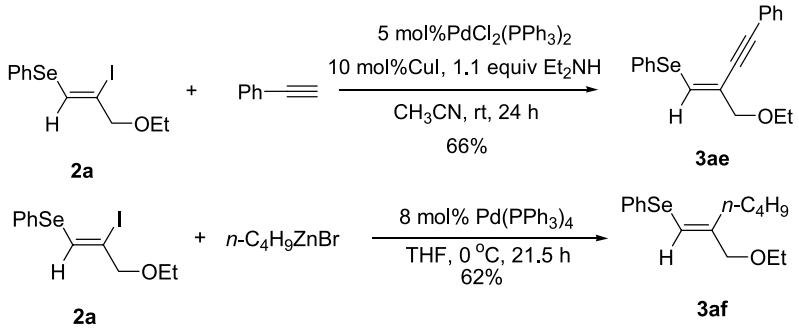


Scheme 4.

Table 3. Suzuki coupling reaction of **2a**



Entry	R	Time (h)	Yield (%)
1	Ph	22.5	79 (**3aa**)
2	4-$MeOC_6H_4$	17.5	76 (**3ab**)
3	4-MeC_6H_4	17.5	75 (**3ac**)
4	4-$MeCOC_6H_4$	22.5	39 (**3ad**)



Scheme 5.

In conclusion, we have shown that the alcohol can act as a nucleophile in electrophilic addition of I_2 with 1,2-allenyl selenides or sulfides. Due to the high stereoselectivity and easy availability of starting materials, this method further expanded the scope of the stereoselective electrophilic addition of 1,2-allenyl sulfides or selenides with halogen. Further studies in this area, are being carried out in our laboratory.

3. Experimental

3.1. Typical procedure for the synthesis of 2a

A solution of **1a** (50.4 mg, 0.26 mmol) and iodine (128.3 mg, 0.5 mmol) in 5 mL of MeCN and 0.25 mL of EtOH (20:1) was stirred at room temperature for 1 h. The mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$. The mixture was then extracted with diethyl ether (25 mL×3) and dried over anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate 200:1) afforded **2a** (64.7 mg, 68%) as a liquid.

3.1.1. Synthesis of (*Z*)-3-ethoxy-2-iodopropenyl phenyl selenide (2a). The reaction of 50.4 mg (0.26 mmol) of **1a** and 128.3 mg (0.51 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of EtOH (20:1) afforded 64.7 mg (68%) of **2a**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.35 (s, 1H), 7.27–7.19 (m, 3H), 4.04 (s, 2H), 3.42 (q, J=7.0 Hz, 2H), 1.16 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 133.5, 129.5, 129.4, 128.1, 102.4, 78.7, 65.4, 15.1; MS (70 eV, EI) *m*/*z* (%): 368 (M^+(^{80}Se), 35.40), 366 (M^+(^{78}Se), 18.46), 83 (100); IR ν (cm^{-1}): 3056, 1580, 1476, 1439, 1104, 737. Anal. Calcd for $C_{11}H_{13}IOSe$: C, 35.99; H, 3.57. Found: C, 36.29; H, 3.53.

3.1.2. Synthesis of (*Z*)-3-isobutoxy-2-iodopropenyl phenyl selenide (2b). The reaction of 51.5 mg (0.26 mmol) of **1a** and 123.6 mg (0.49 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of *i*-butanol (20:1) afforded 65.4 mg (63%) of **2b**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.43 (s, 1H), 7.34–7.32 (m, 3H), 4.11 (s, 2H), 3.20 (d, J=6.4 Hz, 2H), 1.91–1.87 (m, 1H), 0.95 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5, 133.4, 129.5, 129.4, 128.0, 102.7, 78.9, 76.7, 28.4, 19.4; MS (70 eV, EI) *m*/*z* (%): 396

(M^+(^{80}Se), 8.45), 394 (M^+(^{78}Se), 4.83), 57 (100); IR (neat) ν (cm^{-1}): 2955, 2870, 1578, 1475, 1438, 1103, 737; HRMS calcd for $C_{13}H_{17}IO^{80}Se$: 395.9489. Found: 395.9475.

3.1.3. Synthesis of (*Z*)-3-pentoxy-2-iodopropenyl phenyl selenide (2c). The reaction of 52.4 mg (0.27 mmol) of **1a** and 130.3 mg (0.51 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of pentanol (20:1) afforded 83.1 mg (76%) of **2c**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.42 (s, 1H), 7.34–7.32 (m, 3H), 4.10 (s, 2H), 3.41 (t, J=6.4 Hz, 2H), 1.61–1.58 (m, 2H), 1.35–1.32 (m, 4H), 0.89 (t, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.54, 133.49, 129.5, 129.4, 128.1, 102.6, 78.9, 70.1, 29.3, 28.3, 22.5, 14.0; MS (70 eV, EI) *m/z* (%): 410 (M^+(^{80}Se), 14.32), 408 (M^+(^{78}Se), 8.24), 43 (100); IR (neat) ν (cm^{-1}): 2954, 2930, 2858, 1578, 1476, 1105, 736; HRMS calcd for $C_{14}H_{19}IO^{80}Se$: 409.9646. Found: 409.9675.

3.1.4. Synthesis of (*Z*)-3-cyclohexoxy-2-iodopropenyl phenyl selenide (2d). The reaction of 47.2 mg (0.25 mmol) of **1a** and 131.4 mg (0.5 mmol) of I_2 in 5 mL of MeCN and 0.3 mL of cyclohexanol (20:1) afforded 81.5 mg (80%) of **2d**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2H), 7.42 (s, 1H), 7.33–7.31 (m, 3H), 4.14 (s, 2H), 3.36–3.32 (m, 1H), 1.89–1.86 (m, 2H), 1.75–1.71 (m, 2H), 1.53–1.51 (m, 1H), 1.34–1.21 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4, 132.7, 129.7, 129.4, 128.0, 103.5, 76.9, 76.1, 32.2, 25.7, 24.0; MS (70 eV, EI) *m/z* (%): 422 (M^+(^{80}Se), 15.98), 420 (M^+(^{78}Se), 9.07), 55 (100); IR (neat) ν (cm^{-1}): 2930, 2854, 1578, 1477, 1438, 1098, 736, 690; HRMS for $C_{15}H_{19}IO^{80}Se$: 421.9646. Found: 421.9686.

3.1.5. Synthesis of (*Z*)-3-benzoxy-2-iodopropenyl phenyl selenide (2e). The reaction of 47.1 mg (0.25 mmol) of **1a** and 132.4 mg (0.5 mmol) of I_2 in 5 mL of MeCN and 0.3 mL of benzyl alcohol (20:1) afforded 79.5 mg (77%) of **2e**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.48 (s, 1H), 7.37–7.30 (m, 8H), 4.54 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.5, 133.6, 133.5, 129.5, 128.4, 128.1, 127.9, 127.8, 101.8, 78.0, 71.5; MS (70 eV, EI) *m/z* (%): 430 (M^+(^{80}Se), 4.37), 428 (M^+(^{78}Se), 2.43), 91 (100); IR (neat) ν (cm^{-1}): 2855, 1578, 1496, 1438, 1096, 735, 692; HRMS calcd for $C_{16}H_{15}IO^{80}Se$: 429.9333. Found: 429.9377.

3.1.6. Synthesis of (*Z*)-3-ethoxy-2-iodopropenyl benzyl selenide (2f). The reaction of 52.9 mg (0.26 mmol) of **1c** and 128.3 mg (0.5 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of EtOH (20:1) afforded 61.0 mg (64%) of **2f**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.23 (m, 4H), 7.17–7.15 (m, 2H), 3.96 (s, 4H), 3.33 (q, J=7.2 Hz, 2H), 1.12 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 131.0, 128.8, 128.7, 127.2, 102.6, 78.7, 65.2, 29.8, 15.0; MS (70 eV, EI) *m/z* (%): 382 (M^+(^{80}Se), 3.7), 380 (M^+(^{78}Se), 1.5), 91 (100); IR ν (cm^{-1}): 2972, 2926, 2868, 1584, 1494, 1453, 1103, 697; HRMS calcd for $C_{12}H_{15}IO^{80}Se$: 381.9333. Found: 381.9360.

3.1.7. Synthesis of (*Z*)-3-ethoxy-2-iodopropenyl phenyl sulfide (2g). The reaction of 74.6 mg (0.50 mmol) of **1b** and 259.4 mg (1.02 mmol) of I_2 in 8 mL of MeCN and 0.4 mL of EtOH (20:1) afforded 79.0 mg (49%) of **2g**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=1.2 Hz, 2H), 7.36–7.29 (m, 3H), 7.03 (s, 1H), 4.16 (d, J=1.2 Hz, 2H), 3.50 (q, J=7.2 Hz, 2H), 1.23 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 133.9, 130.8, 129.3, 127.7, 98.7, 78.1, 65.4, 15.1; MS (70 eV, EI) *m/z* (%): 320 (M^+, 36.38), 83 (100); IR (neat) ν (cm^{-1}): 2974, 2926, 2869, 1578, 1476, 1439, 1105, 742, 691; HRMS calcd for $C_{11}H_{13}IOS$: 319.9732. Found: 319.9750.

3.1.8. Synthesis of (*Z*)-3-(3′-butyn-2′-oxy)-2-iodopropenyl phenyl selenide (2h). The reaction of 49.1 mg (0.25 mmol) of **1a** and 131.7 mg (0.51 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of but-3-yn-2-ol (20:1) afforded 60.1 mg (61%) of **2h**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 2H), 7.49 (s, 1H), 7.34–7.32 (m, 3H), 4.31 (d, J=13.0 Hz, 1H), 4.22 (d, J=13.0 Hz, 1H), 4.23–4.20 (m, 1H), 2.42 (s, 1H), 1.48 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.5, 129.5, 129.4, 128.1, 101.0, 82.9, 76.4, 73.5, 63.6, 21.9; MS (70 eV, EI) *m/z* (%): 392 (M^+(^{80}Se), 29.35), 390 (M^+(^{78}Se), 15.77), 53 (100); IR (neat) ν (cm^{-1}): 3292, 2986, 2109, 1577, 1099, 739; HRMS calcd for $C_{13}H_{13}IO^{80}SeNa^+$: 414.9069. Found: 414.9077.

3.1.9. Synthesis of (*Z*)-3-(hept-2′-ynoxy)-2-iodopropenyl phenyl selenide (2i). The reaction of 47.1 mg (0.25 mmol) of **1a** and 127.1 mg (0.50 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of Hept-2-yn-1-ol (20:1) afforded 61.2 mg (58%) of **2i**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 2H), 7.49–7.48 (m, 1H), 7.33–7.31 (m, 3H), 4.22 (s, 2H), 4.15 (s, 2H), 2.20 (t, J=6.8 Hz, 2H), 1.49–1.35 (m, 4H), 0.88 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.5, 129.4, 128.1, 100.7, 87.8, 77.0, 75.1, 57.1, 30.6, 21.9, 18.4, 13.5; MS (70 eV, EI) *m/z* (%): 434 (M^+(^{80}Se), 2.1), 432 (M^+(^{78}Se), 1.2), 235 (100); IR (neat) ν (cm^{-1}): 2956, 2930, 2221, 1578, 1091, 739; HRMS calcd for $C_{16}H_{19}IO^{80}SeNa^+$: 456.9544. Found: 456.9555.

3.1.10. Synthesis of (*Z*)-3-alloxy-2-iodopropenyl phenyl selenide (2j). The reaction of 98.8 mg (0.51 mmol) of **1a** and 255.0 mg (1.00 mmol) of I_2 in 8 mL of MeCN and 0.4 mL of allyl alcohol (20:1) afforded 121.5 mg (63%) of **2j**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.44 (s, 1H), 7.35–7.32 (m, 3H), 5.95–5.88 (m, 1H), 5.29 (d, J=18.0 Hz, 1H), 5.20 (d, J=10.4 Hz, 1H), 4.13 (s, 2H), 4.00 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.11, 134.07, 133.5, 129.5, 129.4, 128.1, 117.6, 101.7, 78.0, 70.6; MS (70 eV, EI) *m/z* (%): 380 (M^+(^{80}Se), 18.11), 378 (M^+(^{78}Se), 9.41), 41 (100); IR (neat) ν (cm^{-1}): 2924, 2852,

1645, 1578, 1477, 1438, 1095, 1022, 738. Anal. Calcd for $C_{12}H_{13}IOSe$: C, 38.02; H, 3.46. Found: C, 38.28; H, 3.61.

3.1.11. Synthesis of (*Z*)-3-alloxy-2-iodopropenyl phenyl sulfide (2k). The reaction of 82.1 mg (0.55 mmol) of **1b** and 255.5 mg (1.01 mmol) of I_2 in 8 mL of MeCN and 0.4 mL of allyl alcohol (20:1) afforded 74.4 mg (40%) of **2k**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.44 (m, 2H), 7.36–7.28 (m, 3H), 7.06 (s, 1H), 5.96–5.89 (m, 1H), 5.31 (d, J=17.6 Hz, 1H), 5.21 (d, J=10.0 Hz, 1H), 4.19 (s, 2H), 4.01 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 134.1, 133.7, 130.8, 129.2, 127.7, 117.6, 97.9, 77.3, 70.6; MS (70 eV, EI) *m*/*z* (%): 332 (M^+, 28.53), 41 (100); IR (neat) ν (cm^{-1}): 2852, 1646, 1581, 1477, 1440, 1097, 743, 691; HRMS calcd for $C_{12}H_{13}IOS$: 331.9732. Found: 331.9688.

3.1.12. Synthesis of (*Z*)-3-(prop-2′-ynoxy)-2-iodopropenyl phenyl selenide (2m). The reaction of 53.8 mg (0.28 mmol) of **1a** and 129.8 mg (0.51 mmol) of I_2 in 5 mL of MeCN and 0.25 mL of prop-2-ynol (20:1) afforded 53.1 mg (51%) of **2m**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.51 (s, 1H), 7.35–7.33 (m, 3H), 4.24 (s, 2H), 4.17 (d, J=2.4 Hz, 2H), 2.44 (t, J=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 133.6, 129.5, 129.4, 128.2, 100.0, 79.0, 77.3, 75.1, 56.5; MS (70 eV, EI) *m*/*z* (%): 378 (M^+(^{80}Se), 40.63), 376 (M^+(^{78}Se), 20.66), 221 (100); IR (neat) ν (cm^{-1}): 3292, 2361, 1579, 1476, 1439, 1348, 1095, 738. Anal. Calcd for $C_{12}H_{11}IOSe$: C, 38.22; H, 2.94. Found: C, 38.39; H, 3.02.

3.1.13. Synthesis of (*Z*)-3-alloxy-2-iodopropenyl benzyl selenide (2n). The reaction of 87.1 mg (0.42 mmol) of **1c** and 222.1 mg (0.87 mmol) of I_2 in 8 mL of MeCN and 4 mL of allyl alcohol (20:1) afforded 49.8 mg (30%) of **2n**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 6H), 5.92–5.85 (m, 1H), 5.24 (d, J=17.6 Hz, 1H), 5.20 (d, J=10.4 Hz, 1H), 4.07 (s, 2H), 4.05 (s, 2H), 3.93 (d, J=5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 134.1, 131.6, 128.8, 128.7, 127.2, 117.6, 101.9, 77.9, 70.4, 29.8; MS (70 eV, EI) *m*/*z* (%): 394 (M^+(^{80}Se), 2.1), 392 (M^+(^{78}Se), 1.1), 91 (100); IR ν (cm^{-1}): 3026, 2852, 1646, 1583, 1494, 1453, 1183, 1094, 759, 697; HRMS calcd for $C_{13}H_{15}IO^{80}Se$: 393.9333. Found: 393.9367.

3.1.14. Synthesis of (*Z*)-3-(prop-2′-ynoxy)-2-iodopropenyl benzyl selenide (2o). The reaction of 86.1 mg (0.41 mmol) of **1c** and 205.2 mg (0.81 mmol) of I_2 in 8 mL of MeCN and 0.4 mL of prop-2-ynol (20:1) afforded 41.1 mg (26%) of **2o**: liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.19 (m, 6H), 4.13 (s, 2H), 4.05 (d, J=2.4 Hz, 2H), 4.01 (s, 2H), 2.39 (t, J=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 133.5, 128.6, 128.5, 127.1, 100, 1, 78.8, 76.5, 74.8, 56.0, 29.7; MS (70 eV, EI) *m*/*z* (%): 392 (M^+(^{80}Se), 1.1), 390 (M^+(^{78}Se), 0.5), 91 (100); IR ν (cm^{-1}): 3291, 2849, 2247, 1582, 1494, 1453, 1095, 1047, 732, 697; HRMS calcd for $C_{13}H_{13}IO^{80}Se$: 391.9176. Found: 391.9176.

3.1.15. Synthesis of (*E*)-3-ethoxy-2-phenylpropenyl phenyl selenide (3aa). The reaction of 100.6 mg (0.27 mmol) of **2a**, phenyl boronic acid (60.6 mg, 0.51 mmol), $Pd(PPh_3)_4$ (14.7 mg, 5 mol%), CH_3OH (0.1 mL) and Na_2CO_3 (0.3 mL, 2 M in H_2O) in 2 mL of toluene was refluxed under N_2 for 22.5 h as monitored by TLC (petroleum ether/ethyl acetate 40:1). Water (10 mL) was added and the reaction mixture was extracted with ether, washed with saturated NaCl, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel afforded 68.5 mg (79%) of **3aa** as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.42–7.41 (m, 4H), 7.34–7.29 (m, 4H), 6.84 (s, 1H), 4.30 (s, 2H), 3.56 (q, J=7.0 Hz, 2H), 1.21 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.9, 132.4, 131.3, 129.2, 128.4, 127.8, 127.6, 127.3, 122.3, 74.8, 65.5, 15.1; MS (70 eV, EI) *m*/*z* (%): 318 (M^+(^{80}Se), 56.16), 316 (M^+(^{78}Se), 29.21), 133 (100); IR (neat) ν (cm^{-1}): 2973, 2926, 2866, 1578, 1158, 1098, 697; HRMS calcd for $C_{17}H_{19}O^{80}Se^+$ (M^++H): 319.0596. Found: 319.0593.

3.1.16. Synthesis of (*E*)-3-ethoxy-2-(4′-methoxyphenyl) propenyl phenyl selenide (3ab). The reaction of 88.9 mg (0.24 mmol) of **2a**, *p*-methoxy-phenyl boronic acid (72.6 mg, 0.48 mmol), $Pd(PPh_3)_4$ (15.1 mg, 5 mol%), CH_3OH (0.1 mL) and Na_2CO_3 (0.3 mL, 2 M in H_2O) in 2 mL of toluene afforded 64.2 mg (76%) of **3ab** as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.36–7.26 (m, 5H), 6.95 (d, J=8.4 Hz, 2H), 6.77 (s, 1H), 4.28 (s, 2H), 3.84 (s, 3H), 3.54 (q, J=7.1 Hz, 2H), 1.21 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.8, 132.4, 131.4, 131.1, 129.1, 128.9, 127.2, 121.4, 113.7, 74.9, 65.4, 55.1, 15.1; MS (70 eV, EI) *m*/*z* (%): 348 (M^+(^{80}Se), 94.27), 346 (M^+(^{78}Se), 48.73), 163 (100); IR (neat) ν (cm^{-1}): 2972, 1607, 1510, 1248; HRMS calcd for $C_{18}H_{21}O_2^{80}Se^+$ (M^++H): 349.0701. Found: 349.0702.

3.1.17. Synthesis of (*E*)-3-ethoxy-2-(4′-methylphenyl) propenyl phenyl selenide (3ac). The reaction of 88.3 mg (0.24 mmol) of **2a**, *p*-methylphenyl boronic acid (66.3 mg, 0.49 mmol), $Pd(PPh_3)_4$ (18.4 mg, 6 mol%), CH_3OH (0.1 mL) and Na_2CO_3 (0.3 mL, 2 M in H_2O) in 2 mL of toluene was afforded 59.9 mg (75%) of **3ac** as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.31–7.22 (m, 7H), 6.81 (s, 1H), 4.29 (s, 2H), 3.55 (q, J=7.0 Hz, 2H), 2.39 (s, 3H), 1.21 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.6, 135.9, 132.4, 131.4, 129.14, 129.11, 127.5, 127.2, 121.6, 74.8, 65.5, 21.3, 15.1; MS (70 eV, EI) *m*/*z* (%): 332 (M^+(^{80}Se), 100), 330 (M^+(^{78}Se), 51.40); IR (neat) ν (cm^{-1}): 2973, 2865, 1578, 1511, 1120, 737; HRMS calcd for $C_{18}H_{21}O^{80}Se^+$ (M^++H): 333.0752. Found: 333.0748.

3.1.18. Synthesis of (*E*)-3-ethoxy-2-(4′-acetylphenyl)propenyl phenyl selenide (3ad). The reaction of 96.9 mg (0.26 mmol) of **2a**, *p*-acetylphenyl boronic acid (86.4 mg, 0.53 mmol), $Pd(PPh_3)_4$ (21.6 mg, 6 mol%), CH_3OH (0.1 mL) and Na_2CO_3 (0.3 mL, 2 M in H_2O) in 2 mL of toluene afforded 36.9 mg (39%) of **3ad** as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J=8.4 Hz, 2H), 7.55–7.50 (m, 4H), 7.31–7.30 (m, 3H), 6.92 (s, 1H), 4.29 (s, 2H), 3.52 (q, J=7.0 Hz, 2H), 2.62 (s, 3H), 1.18 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 143.8, 138.0, 136.2, 132.7, 130.8, 129.3, 128.5, 127.9, 127.6, 124.9, 74.7, 65.6, 26.6, 15.1; MS (70 eV, EI) *m/z* (%): 360 (M^+(^{80}Se), 96.22), 358 (M^+(^{78}Se), 49.10), 115 (100); IR (neat) ν (cm^{-1}): 2973, 2866, 1683, 1603, 1578, 1266, 1095, 847, 739, 691; HRMS calcd for $C_{19}H_{21}O_2^{80}Se^+$ (M^++H): 361.0701. Found: 361.0719.

3.1.19. Synthesis of (*E*)-3-ethoxy-2-(phenylethynyl)propenyl phenyl selenide (3ae). A mixture of 87.3 mg (0.24 mmol) of **2a**, phenylacetylene (38.9 mg, 0.38 mmol), Et_2NH (21.1 mg, 0.289 mmol), CuI (5.7 mg, 10 mol%), and $PdCl_2(PPh_3)_2$ (8.6 mg, 5% mol) in 2.5 mL of CH_3CN was stirred at room temperature under N_2 for 24 h as monitored by TLC (petroleum ether/ethyl acetate 40:1). Water (10 mL) was added and the reaction mixture was extracted with ether. The combined extracts were washed with saturated NaCl and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate 200:1) afforded 53.7 mg (66%) of **3ae** as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.54–7.53 (m, 2H), 7.34–7.33 (m, 6H), 7.11 (s, 1H), 4.11 (s, 2H), 3.59 (q, J=6.8 Hz, 2H), 1.25 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 133.0, 131.6, 130.0, 129.3, 128.4, 128.2, 127.7, 122.9, 120.9, 97.1, 86.4, 73.1, 65.8, 15.1; MS (70 eV, EI) *m/z* (%): 342 (M^+(^{80}Se), 100), 340 (M^+(^{78}Se), 51.49); IR (neat) ν (cm^{-1}): 2974, 2866, 2186, 1597, 1094, 755, 690; HRMS calcd for $C_{19}H_{19}O^{80}Se^+$ (M^++H): 343.0596. Found: 343.0596.

3.1.20. Synthesis of (*E*)-3-ethoxy-2-butylpropenyl phenyl selenide (3af). To a solution of anhydrous $ZnBr_2$ (145.4 mg, 0.65 mmol) in 1.5 mL of THF was added dropwise *n*-C_4H_9Li (0.18 mL, 2.88 M in hexane) at 0 °C. After stirring for 10 min, $Pd(PPh_3)_4$ (20.2 mg, 8 mol%) and a 1.5 mL of THF solution of 79.0 mg (0.22 mmol) of **2a** were added and the mixture was stirred for 21.5 h as monitored by TLC (petroleum ether/ethyl acetate 40:1). Water (10 mL) was added and the reaction mixture was extracted with ether, washed with saturated NaCl, and dried over Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel afforded 39.8 mg (62%) of **3af** as an oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J=7.6 Hz, 2H), 7.28–7.23 (m, 3H), 6.45 (s, 1H), 3.97 (s, 2H), 3.46 (q, J=6.8 Hz, 2H), 2.23 (t, J=7.2 Hz, 2H), 1.47–1.33 (m, 4H), 1.20 (t, J=6.8 Hz, 3H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 131.8, 131.2, 129.1, 126.8, 117.5, 73.8, 65.4, 31.7, 30.0, 22.7, 15.1, 14.0; MS (70 eV, EI) *m/z* (%): 298 (M^+(^{80}Se), 53.17), 296 (M^+(^{78}Se), 26.74), 85 (100); IR (neat) ν (cm^{-1}): 2957, 2928, 2858, 1579, 1477, 1438, 1119, 1096, 735, 690; HRMS calcd for $C_{15}H_{23}O^{80}Se^+$ (M^++H): 299.0909. Found: 299.0898.

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