Synthesis of Alkynyl and Vinyl Selenides via Selenodecarboxylation of Arylpropiolic and Cinnamic Acids

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The selenodecarboxylation of phenylpropiolic and cinnamic acid derivatives with diorgano diselenide is promoted by iodosobenzene diacetate ($PhI(OAc)_2$, IBDA) in acetonitrile at 30−60 °C, leading to the formation of alkynyl selenides and vinyl selenides in moderate to excellent yields. Similar reactivity is also shown by iodosylbenzene (PhIO, IB). The reaction is also triggered in the solid state. An electrophilic mechanism is proposed for the transformation.

Alkynyl and vinyl selenides play an important role in organic synthesis by serving as crucial synthons in the transformations of a variety of functional groups with a high degree of selectivity.[1,2] Alkynyl selenides are often sought to transform to corresponding functionalized vinyl selenides by chlorocarbonylation, hydrohalogenation, hydrosulfonation, and hydrometalation.[3] Additionally, they have been demonstrated to perform as excellent Diels−Alder dienophiles[4] and as inhibitors of oxidative enzymes such as δ-aminolevulinate dehydratase.[5] On the other hand, vinyl selenides are gaining usage in the stereoselective construction of functionalized alkenes via organometallic cross-coupling reactions.[6] They are also emerging as interesting candidates in cycloaddition reactions[7] and as direct precursors to vinyl stannanes.[8]

Major routes to alkynyl and vinyl selenides include (a) reaction of corresponding halides or surrogates with nucleophilic selenium (RSeM),[9] (b) reaction of alkynyl and vinyl organometallics with organoselenenyl halide (RSeX) or diorgano diselenides (RSeSeR),[10] (c) Horner−Emmons or Wittig olefination of α-seleno phosphonates or α-acyl-α-seleno phosphoranes,[11] and (d) selenofunctionalization of alkenes, alkynes, and allenes.[12] In a conceptually different strategy, we sought to find a gateway into alkynyl and vinyl selenides directly from the corresponding unsaturated acids via selenodecarboxylation reaction. In this regard the elegant example of selenodecarboxylation by Barton's reagent is noteworthy, which makes use of the reaction of diaryl diselenides with *O*-acyl thiohydroxamates generated in situ from aliphatic and alicyclic carboxylic acids.[13]

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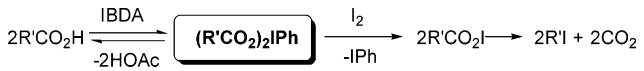
Scheme 1



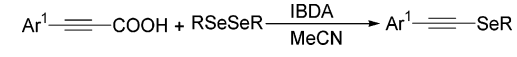
However, to our knowledge, selenodecarboxylation of unsaturated acids is not observed yet. In this paper we delineate a facile selenodecarboxylation reaction of arylpropiolic and cinnamic acid derivatives using iodosobenzene diacetate or iodosylbenzene and diaryl diselenides under thermal conditions in solution as well as solid phase.

The present study originated from our continuing success in decarboxylative ipso-substitution reactions of aromatic α,β-unsaturated acids and ongoing interest in seleno-transfer reactions.[14,15] In earlier studies we have shown that halodecarboxylations are promoted by halogenium ion, whereas nitrodecarboxylation follows a radical pathway. In accordance with this knowledge, we initially explored selenodecarboxylation with both organoselenyl cations and organoselenyl radicals (discussed in the Supporting Information and Tables S1, S2). Reactions under radical conditions did not give any trace of product. Although electrophilic selenium reagents promoted decarboxylation, the desired product was obtained in low yields (up to 25%). This prompted us to look for alternate reagent combinations, which culminated into a successful introduction of hypervalent aryliodonium carboxylates as a new reagent for selenodecarboxylation.

Hypervalent iodine reagents are gaining meaningful entry in organic synthesis.[16] We became particularly interested in iodosobenzene diacetate (IBDA), in view of earlier reports on the halodecarboxylation of saturated and unsaturated carboxylic acids using reagent combinations (IBDA)/I_2/$h\nu$/CCl_4, IBDA/LiCl, and IBDA/NBS.[17] In these cases intermediacy of a new complex of the type $(R'CO_2)_2IPh$ had been postulated prior to halodecarboxylation (Scheme 1). Also noteworthy are reports on the utilization of IBDA/ArSeSeAr or PhI(OTf)$_2$/ArSeSeAr for phenylselenoacetoxylation of alkenes, lactonization of γ,δ-unsaturated acids, selenenylation of terminal alkynes, and synthesis of phosphoroselenoates and selenosulfonates.[18]

The reaction of arylpropiolic acids with diaryl diselenide and IBDA resulted in clean reactions affording the corresponding alkynyl selenides in good to excellent yields (Table 1). Thus reaction of phenylpropiolic acid **1** (1 mmol) with diphenyl diselenide (0.3 mmol) and IBDA (0.5 mmol) in acetonitrile (3 mL) at room temperature led to 1-phenylseleno-2-phenylacetylene (**1a**) in 84% isolated yield after 6 h (entry 1). Moreover, the yields were nearly unaffected in reactions conducted in the presence of oxygen or *N*-α-diphenylnitrone as a radical trap, which excludes a radical pathway (entries 2, 3). Similar reaction with ditolyl diselenide (RSeSeR, where R = Tol) afforded 1-tolylseleno-2-phenylacetylene (**1b**) in 86% yield (entry 4). Both electron-withdrawing and -donating substituents could be tolerated in the phenyl ring, as evident from the reaction of acids **2** and **3**. Thus 4-methoxyphenylpropiolic acid **2** afforded the corresponding (aryl)alkynyl selenides **2a** and **2b** in 90 and 88% yield, respectively (entries 5, 6). Whereas in the case of a ring-deactivated arylpropiolic acid such as 4-chlorophenylpropiolic acid **3**, the corresponding selenodecarboxylated products **3a** and **3b** were obtained in 66 and 75% yields, respectively (entries 7, 8). Propiolic acids **4** and **5**, bearing thienyl and naphthyl appendages, were also found effective, providing the desired selenides in 60−90% yields (entries 9−11). Note that we have added an excess acid to obviate an operational difficulty with respect to TLC visualization;[19] the excess acid can be isolated satisfactorily after workup.

Table 1. Selenodecarboxylation of Arylpropiolic Acids to Alkynyl Selenides[a]



entry	acid no.	Ar^1	R	pdt. no.	time (h)	yield (%)
1	**1**	Ph	Ph	**1a**	6	84
2[b]	**1**	Ph	Ph	**1a**	6	80
3[c]	**1**	Ph	Ph	**1a**	6	78
4	**1**	Ph	Tol	**1b**	6	86
5	**2**	4-MeO-C_6H_4	Ph	**2a**	5	90
6	**2**	4-MeO-C_6H_4	Tol	**2b**	5	88
7	**3**	4-Cl-C_6H_4	Ph	**3a**	7	66
8	**3**	4-Cl-C_6H_4	Tol	**3b**	7	75
9	**4**	2-thienyl	Ph	**4a**	7	60
10	**4**	2-thienyl	Tol	**4b**	6	65
11	**5**	1-naphthyl	Ph	**5a**	5	90

[a] Conditions: acid (1 mmol), IBDA (0.5 mmol), RSeSeR (0.3 mmol), solvent MeCN, 30 °C. [b] In the presence of 20% *N*-α-diphenylnitrone as radical trap. [c] In the presence of oxygen.

The success in the selenodecarboxylation of arylpropiolic acids prompted us to test the reaction for cinnamic acids. In this case, the selenodecarboxylation was found to be facile for acids bearing electron-donating groups in the phenyl ring, giving rise to the corresponding (*E*)-vinyl selenides in moderate yields (Table 2). However, when compared to arylpropiolic acid, the reactions are

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(19) When visualized under UV, both alkynyl selenide and ArSeSeAr showed nearly overlapping spots (similar R_f values). Fortunately, under tungsten lamp illumination, the product was found to be colorless, while the diselenide showed an intense yellow spot. Hence, full conversion is judged by the complete disappearance of the yellow spot due to ArSeSeAr. Note that even traces of diselenide present in the mixture show quite intense yellow spots, posing difficulty in judging the conversion. We believe that any one monitoring the reaction by HPLC or 2D-TLC would be able to carry out the decarboxylation under ideal stoichiometry.

Table 2. Selenodecarboxylation of Cinnamic Acids to (*E*)-Vinyl Selenides[a]

$Ar^2CH{=}CH\text{-}COOH + RSeSeR \xrightarrow[MeCN]{IBDA} Ar^2CH{=}CH{-}SeR$

entry	acid no.	Ar^2	R	pdt. no.	time (h)	yield (%)
1	**6**	4-MeO-C_6H_4	Ph	**6a**	12	68
2[b]	**6**	4-MeO-C_6H_4	Ph	**6a**	12	65
3[c]	**6**	4-MeO-C_6H_4	Ph	**6a**	12	64
4[d]	**6**	4-MeO-C_6H_4	Ph	**6a**	12	58
5	**6**	4-MeO-C_6H_4	Tol	**6b**	8	62
6	**7**	3,4,5-$(MeO)_3$-C_6H_2	Ph	**7a**	14	55
7	**7**	3,4,5-$(MeO)_3$-C_6H_2	Tol	**7b**	14	50
8	**8**	3,4-methylene dioxy-C_6H_3	Ph	**8a**	11	53
9	**8**	3,4-methylene dioxy-C_6H_3	Tol	**8b**	15	48
10	**9**	Ph	Ph	**9a**	24	20

[a] Unless otherwise stated the following conditions are used: Acid (1 mmol), IBDA (0.5 mmol), RSeSeR (0.4 mmol), solvent MeCN, 60 °C. [b]RSeSeR (0.5 mmol). [c]In the presence of 20% *N*-α-diphenylnitrone as radical trap. [d]In the presence of oxygen.

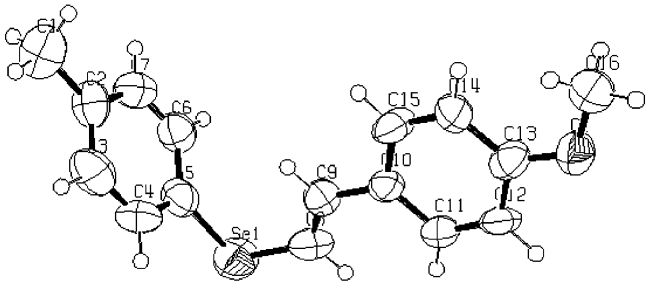
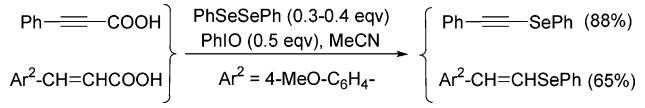


Figure 1. ORTEP diagram of **6b** with 50% probability thermal ellipsoids.

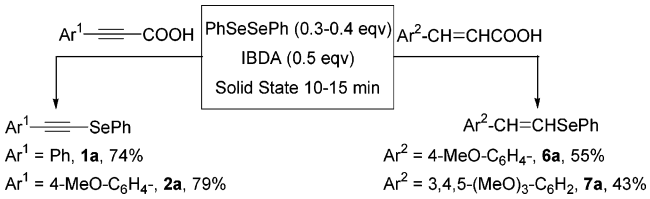
kinetically slower; hence a higher temperature was required to achieve good conversion. Thus reaction of 4-methoxycinnamic acid **6** (1 mmol) with diphenyl diselenide (0.4 mmol) and IBDA (0.5 mmol) in acetonitrile (3 mL) at 60 °C for 12 h afforded (*E*)-(2-(4-methoxyphenyl)vinylseleno)benzene (**6a**) in 68% isolated yield (Table 2, entry 1). The yield was similar at the exact stoichiometric condition acid:IBDA:diselenide = 2:1:1 (Table 2, entry 2). As in the case of arylpropiolic acids, *N*-α-diphenylnitrone or oxygen had no role in the selenodecarboxylation of cinnamic acids (Table 2, entries 3, 4). A similar reaction of acid **6** with ditolyl diselenide afforded the selenodecarboxylated product (*E*)-(2-(4-methoxyphenyl)-vinylseleno)toluene (**6b**) in 62% yield (entry 5). The reaction of highly substituted 3,4,5-trimethoxycinnamic acid (**7**) and 3,4-methylenedioxycinnamic acid (**8**) with diphenyl diselenide and ditolyl diselenides afforded the corresponding selenodecarboxylated products **7a**, **7b**, **8a**, and **8b** in moderate yields (entries 6−9). That ring activation is necessary to trigger decarboxylation is exemplified by the reactions of cinnamic acid and 4-chlorocinnamic acid, which showed poor or no conversion (entry 10). Similarly acrylic acid failed to show selenodecarboxylation.

It is worth noting that in the case of cinnamic acids we have obtained exclusively the (*E*)-vinyl selenides (vide NMR). The crystal structure of **6b** shows *E*-stereochemistry, angles C10−C9−C8 and C9−C8−Se being 127.4° and 127.9°, respectively (Figure 1). Also the angle C5−Se−C8 is 98.3°. Note that the vinyl(C)−Se bond length is shorter (1.870 Å) than the aryl(C)−Se bond (1.903 Å). To test whether the selenodecarboxylation is stereoselective, a mixture of 4-methoxycinnamic acid (*E*:*Z* = 30:70) was reacted with PhSeSePh under our reaction conditions, which afforded the corresponding vinyl selenide, namely, (2-(4-methoxyphenyl)vinylseleno)benzene, as a mixture in which the *E*:*Z* ratio was 66:33 (vide NMR). This establishes that the decarboxylation is preferentially *E*-selective.

Scheme 2



Scheme 3



The selenodecarboxylation is found to be equally facile with iodosylbenzene (PhIO, IB). Reaction of **1** and **6** (1 mmol) with IB (0.5 mmol) and PhSeSePh (0.3 and 0.4 mmol, respectively) in acetonitrile at 30−60 °C yielded the selenides **1a** and **6a** in 88 and 65% yields, respectively (Scheme 2).

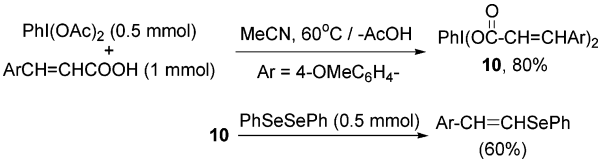
A recent report on the sulfonylation of 1,3-diketones with IBDA and sulfonic acids in the solid state[20] prompted us to test the solid-state reactivity of IBDA in the present selenodecarboxylation reaction. Gratifyingly, simply grinding a mixture of acid with ArSeSeAr and IBDA led to facile reaction within 10−15 min, leading to liquification of the mixture. Extraction of the product into dichloromethane followed by chromatography led to the pure alkynyl or vinyl selenides (Scheme 3).

With regard to the mechanism of selenodecarboxylation, the following observations from control experiments are noteworthy. First, in absence of IBDA or IB no reaction takes place between acids and diorgano diselenides under thermal and photochemical conditions even in the presence of AIBN as initiator.[21] Second, the reaction time and yields of unsymmetrical organo selenides remain unaffected in reactions of acids with ArSeSeAr/IBDA in the presence of a radical trap or oxygen (entries 2, 3 in Table 1, and entries 3, 4 in Table 2). The above observations certainly rule out any radical pathway for the present selenodecarboxylation. To test if any hypervalent iodonium intermediate is involved at the initial stage of the reaction, cinnamic acid **6** was reacted with IBDA (0.5 equiv) in MeCN at 60 °C for 60 min, whereupon a white solid precipitated from the solution. From NMR and analytical data, the solid was identified as the corresponding iodosobenzene dicinnamate $PhI(OOCH{=}CHAr)_2$, **10** (Scheme 4). Cinnamate salt **10** was also isolated from a similar reaction of **6** with IB. Reaction of **10** with PhSeSePh (1 equiv) in MeCN at 60 °C led to the formation of desired selenodecarboxylated product **6a** in 60% yield (Scheme 4).

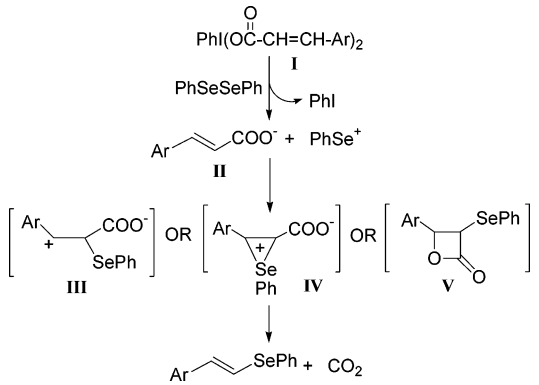
(20) Yusubov, M. S.; Wirth, T. *Org. Lett.* **2005**, *7*, 519.

(21) Generation of $PhSe^{\bullet}$ radical using PhSeSePh/AIBN/*hν* is well known. See: *Organoselenium Chemistry: A Practical Approach*; Back, T. G., Ed.; Oxford University Press: U.K., 1999; Chapter 9.

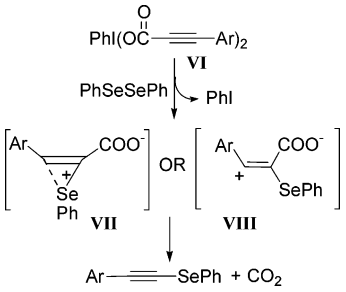
Scheme 4



Scheme 5



Scheme 6



Therefore it appears that the cinnamate (analogously propiolate) salt might be an early intermediate in the selenodecarboxylation pathway.

Even though the exact delineation of the mechanism must await further studies, absence of a radical pathway (discussed earlier) and the susceptibility of selenodecarboxylation with $PhSe^+$-generating agents (discussed in the Supporting Information) lead us to speculate an electrophilic pathway (Schemes 5 and 6; with PhSeSePh as an example). As shown in Scheme 5, under the oxidative influence of iodine(III) in the dicinnamate salt **I**, PhSeSePh is expected to be conducive toward the formation of $PhSe^+$ species. The mechanistic outline suggests the attack of $PhSe^+$ across the $\pi_{C=C}$ bond in **II** to generate either of the three intermediates, namely, an open benzylic carbocation (**III**), an episelenonium ion (**IV**), or α-selenophenyl-β-lactone (**V**).[22] Facile elimination of carbon dioxide could follow from either of these intermediates to afford vinyl selenide. A proposal for the selenodecarboxylation of arylpropiolate salt is shown in Scheme 6, invoking either of the intermediates **VII** and **VIII**.

Finally, to test the likelihood of an electrophilic selenodecarboxylation mechanism, we wished to subject the reaction to Hammett analysis to determine the reaction constant, i.e., ρ-value.[23] This was attempted by kinetic analysis (details in the Supporting Information) using absorption spectroscopy for the selenodecarboxylation of arylpropiolic acids **1**, **2**, and **3** with IBDA and PhSeSePh in chloroform at a molar ratio of 10:5:1 (acid:IBDA:diselenide). The UV−vis spectra of the product alkynyl selenides show a weak but distinct peak at 313−315 nm, which was selected to monitor the progress of the reaction. IBDA and PhSeSePh are nearly transparent in this region. The data for the first 20% conversion fitted nicely into pseudo-first-order rate plots, from which the rate constants (k) were evaluated (Table 3). A plot of $\log(k_R/k_H)$ linearly correlated with the Hammett σ^+ constants, yielding a ρ-value of −3.2 from the slope (Figure 2). The moderate negative ρ-value further strengthens the suggested electrophilic mechanism in the present selenodecarboxylation.[24] Similar kinetic studies could not be attempted for cinnamic acids due to overlapping peaks of vinyl selenides and PhSeSePh.

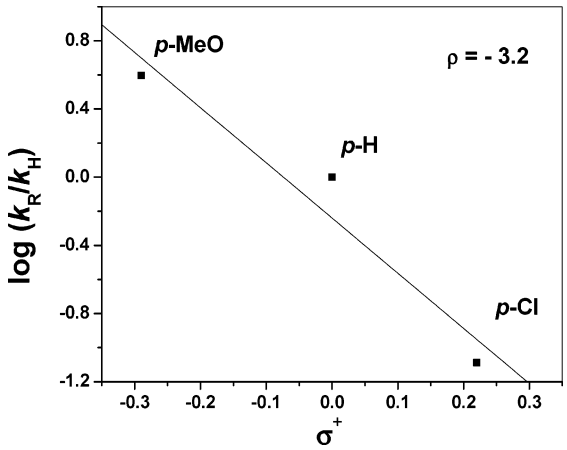


Figure 2. Hammett plot of $\log(k_R/k_H)$ vs σ^+ for selenodecarboxylation of arylpropiolic acids p-R-C_6H_4-C≡C-CO_2H.

Table 3. Kinetic Data for the Selenodecarboxylation of Arylpropiolic Acids with PhSeSePh/IBDA

entry	R	$k_R \times 10^3$ (s^{-1})	k_R/k_H	$\log(k_R/k_H)$	σ^+
1	H	3.7	1	0	0
2	OMe	14.6	3.95	0.59	−0.29
3	Cl	0.3	0.08	−1.08	0.22

In summary, we have shown that facile selenodecarboxylation of arylpropiolic and cinnamic acids can be carried out using ArSeSeAr and IBDA or IB in solution as well as in the solid state. This formal Hunsdiecker-like strategy, which likely involves an electrophilic mechanism, could be a meaningful addition to the existing methods for the synthesis of alkynyl selenides and vinyl selenides. Failure of the reaction with aliphatic acids remains a limitation, which warrants further improvement in reagent and conditions. Studies are underway to look into the above aspects and also to critically examine the selenium-transfer step.

(22) In the case of halodecarboxylation of cinnamic acids with *N*-halosuccinimide, we had earlier observed via semiempirical calculation that the halo-equivalent of episelenonium ion intermediate is more stable over the others. See ref 14, and J. P. Das (doctoral dissertation, IIT Kharagpur, Janurary 2005).

(23) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. In *Organic Chemistry*; Oxford University Press: U.K., 2001; pp 1090−1100.

(24) For electrophilic attack in α,β-unsaturated aromatic systems, a moderately negative ρ-value within −2 to −4 generally implies a transition state in which the positive charge is not far away from the aromatic ring, and there is partial loss of conjugation. See ref 23, and: Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc*. **1968**, *90*, 1020.

Experimental Section.

General Procedures. The following typical procedures have been adopted for the selenodecarboxylation of other acids.

Typical Procedure for the Synthesis of 1-(*p*-Tolylseleno)-2-(*p*-chlorophenyl)acetylene (3b). To a solution of 4-chlorophenylpropiolic acid **3** (181 mg, 1 mmol) in acetonitrile (3 mL) were added IBDA (162 mg, 0.5 mmol) and ditolyl diselenide (102 mg, 0.3 mmol). The reaction mixture was stirred at room temperature for 7 h (TLC monitoring for PhSeSePh, precoated silica gel 60 F_{254} TLC sheets, eluent: *n*-hexane−EtOAc, 9:1). Then the solvent was removed under reduced pressure, and the mixture was subjected to column chromatography over silica gel (100−200 mesh, eluent: hexane) to afford 1-(*p*-tolylseleno)-2-(*p*-chlorophenyl)acetylene (**3b**) in 75% (138 mg) yield with respect to ditolyl diselenide. ^{1}H NMR ($CDCl_3$) δ: 2.34 (s, 3H, $-CH_3$), 7.15 (d, 2H, J = 8 Hz, H_d), 7.28 (d, 2H, J = 9 Hz, H_b), 7.39 (d, 2H, J = 9 Hz, H_a), 7.47 (d, 2H, J = 8 Hz, H_c). ^{13}C NMR ($CDCl_3$) δ: 21.01, 71.25, 100.97, 121.75, 124.59, 128.62, 129.68, 130.38, 132.82, 134.42, 137.42. ESI-MS: for $C_{15}H_{11}ClSe$ [M], $[M + H]^+$ = 306.98 (^{35}Cl) and 308.98 (^{37}Cl), $[M + H - Cl]^+$ = 272.01(^{35}Cl) and 270.01(^{37}Cl), $[M + MeCN + H]^+$ = 348.01(^{35}Cl) and 350.01-(^{37}Cl). Anal. Calcd for $C_{15}H_{11}ClSe$: C, 58.92; H, 3.60. Found: C, 58.87; H, 3.42.

Typical Procedure for the Synthesis of (*E*)-(2-(*p*-Methoxyphenyl)vinylseleno)benzene (6a). To a solution of *p*-methoxycinnamic acid (178 mg, 1 mmol) in acetonitrile (3 mL) was added IBDA (162 mg, 0.5 mmol), and the solution was stirred for 10 min at 60 °C. Following the addition of diphenyl diselenide (125 mg, 0.4 mmol) the reaction mixture was stirred at 60 °C for 12 h (TLC monitoring for PhSeSePh, precoated silica gel 60 F_{254} TLC sheets, eluent: *n*-hexane−EtOAc, 9:1). After concentrating under reduced pressure the mixture was subjected to column chromatography over silica gel (100−200 mesh, eluent 1% ethyl acetate in hexane) to afford (*E*)-(2-(*p*-methoxyphenyl)vinylseleno)benzene (**6a**) in 68% (157 mg) yield with respect to diphenyl diselenide: light yellow solid, mp 50−51 °C. ^{1}H NMR ($CDCl_3$) δ: 3.81 (s, 3H, $-OCH_3$), 6.86 (d, 2H, J = 9 Hz, H_d), 6.88 (d, 1H, J = 16 Hz, Ha), 7.03 (d, 1H, J = 16 Hz, H_b), 7.25−7.34 (m, 3H−Ph + 2H−H_c), 7.49−7.56 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) δ: 55.28, 114.06, 115.90, 127.10, 127.37, 129.24, 129.87, 130.73, 131.99, 135.87, 159.35. ESI-MS: for $C_{15}H_{14}OSe$ [M], $[M]^+$ = 290.04. Anal. Calcd for $C_{15}H_{14}OSe$: C, 62.28; H, 4.84. Found: C, 62.40; H, 4.73.

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Supporting Information Available: General methods, experimental procedures, and spectroscopic, crystallographic, and analytical data/tables/figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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