JOC The Journal of Organic Chemistry

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Solvent-Controlled Halo-Selective Selenylation of Aryl Halides Catalyzed by Cu(II) Supported on Al_2O_3. A General Protocol for the Synthesis of Unsymmetrical Organo Mono- and Bis-Selenides

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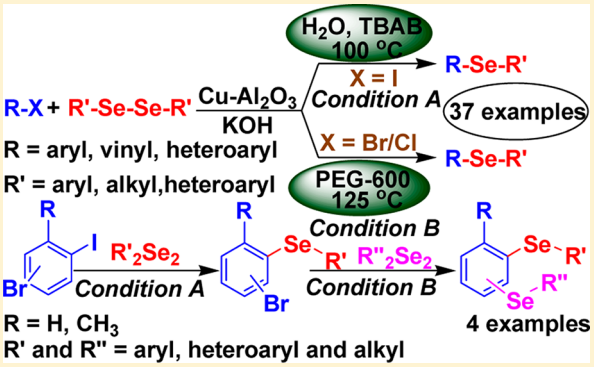
Supporting Information

ABSTRACT: Alumina-supported Cu(II) efficiently catalyzes selenylation of aryl iodides and aryl bromides by diaryl, dialkyl, and diheteroaryl diselenides in water and PEG-600, respectively, leading to a general route toward synthesis of unsymmetrical diaryl, aryl–alkyl, aryl–heteroaryl, and diheteroaryl selenides. A sequential reaction of bromoiodobenzene with one diaryl/diheteroaryl/dialkyl diselenide in water and another diaryl/diheteroaryl/dialkyl diselenide in PEG-600 in the second step produces unsymmetrical diaryl, diheteroaryl, or aryl–alkyl bis-selanyl benzene. A library of functionalized organo mono- and bis-selenides, including a potent biologically active molecule and a couple of analogues of bioactive selenides, were obtained in high yields by this protocol. The reactions are chemoselective and high yielding. The Cu-Al_2O_3 catalyst is recycled for seven runs without any appreciable loss of activity.



INTRODUCTION

The organoselenium compounds are of continued interest because of their potential biological activities, such as antiviral, antihypertensive, antioxidant, antimicrobial, and anticancer properties.[1] A few representative molecules, such as compounds **1** (human breast cancer cell growth inhibitor),[1c] **2** (thioredoxin reductase (TR) and glutathione reductase (GR) inhibitor),[1c] **3** (antitumor agent),[1d] **4** (5-LOX (lipoxygenases) inhibitor),[1e] and **5** (retinoic acid receptor (RAR) agonist, 10 times more potent than its sulfur analogue),[1f,g] are outlined in Figure 1.They also play an important role in organic synthesis as useful intermediates[2] and catalysts.[3] They have important applications as materials, too.[4] Thus, development of efficient synthetic methods for these compounds is of much significance. A number of methods have been reported during the past few years. Transition-metal-catalyzed C–Se bond formation is one of the most popular practices for the synthesis of organoselenides. Several metals, Pd,[5] Ni,[6] Fe,[7] and Cu,[8] have been employed to catalyze the reaction of aryl halides/boronic acids and selenol/PhSeNa/diphenyl diselenide for the synthesis of aryl selenides. However, because of the instability and toxicity of selenol or sodium selenate, the commercially available and stable diphenyl diselenide is widely used. Although these methods are quite satisfactory for the routine preparation of diaryl selenides, the syntheses of unsymmetrical diheteroaryl selenides and diaryl/diheteroaryl/aryl–alkyl bis-selenides were not addressed. Morever, many of these procedures involve hazardous solvents and high temperature. The diheteroaryl sulfides were reported to be potential drug molecules[9] and useful material.[10] Thus, it is likely that the selenide counterparts might be of high potential and interest. This prompted us to develop an efficient and general method that should be applicable for the synthesis of all types of organoselenides, including unsymmetrical diaryl/diheteroaryl/aryl–alkyl mono- and bis-selenides.

We recently reported the synthesis of diaryl/aryl–vinyl selenides by the Cu nanoparticle catalyzed selenylation of aryl iodides and vinyl bromides by Ph_2Se_2,[11a] $CuFe_2O_4$ nanoparticle catalyzed coupling of organoboronic acids and diphenyl diselenides,[11b] microwave-assisted reaction of aryl diazonium fluoroborate and diselenides,[11c] and Cu-Al_2O_3-catalyzed electrophilic substitutions in organoboranes, silanes, and stannanes by PhSeBr.[11d] As a part of our continuing activities in this area, we have observed a unique solvent-controlled selenylation of aryl iodides in water and aryl bromides in PEG-600 by diaryl diselenide using our recently developed Cu-Al_2O_3 catalyst[11e] (Scheme 1).

RESULTS AND DISCUSSION

To standardize the reaction conditions, a series of experiments were performed with variation of solvent, additive, temperature, and time for a representative reaction of 4-methoxyphenyl iodide and diphenyl diselenide in the presence of Cu-Al_2O_3 (5 mol %) and KOH. The results are summarized in Table 1. A variety of solvents, including toluene, THF, DMF, NMP, DMSO, DMC, and H_2O, were studied. The best results in

Received: May 15, 2013
Published: June 20, 2013

   dx.doi.org/10.1021/jo401062k | J. Org. Chem. 2013, 78, 7145–7153

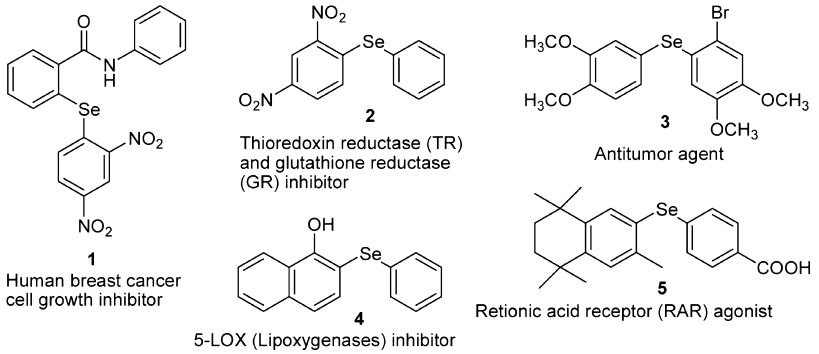


Figure 1. Some biologically active organoselenides.

Scheme 1. Solvent Selective Selenylation of Iodo- and Bromobenzene

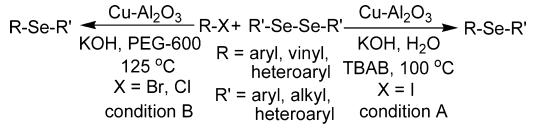
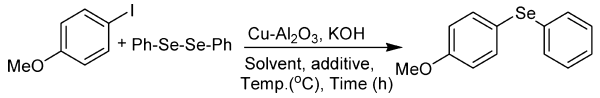


Table 1. Standardization of Reaction Conditions for Selenylation of Iodobenzene



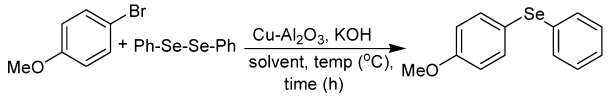
entry	solvent	additive	temp (°C)	time (h)	yield[a] (%)
1	toluene		100	12	10
2	THF		65	12	
3	DMF		110	12	79
4	NMP		110	12	71
5	DMSO		110	12	77
6	DMC		90	12	62
7	H_2O		100	12	66
8	H_2O	TBAB	100	12	84
9	H_2O	SDS	100	12	72
10	H_2O	TBAB	80	12	61
11	**H_2O**	**TBAB**	**100**	**10**	**84**
12	H_2O	TBAB	100	8	70
13[b]	H_2O	TBAB	100	10	63

[a]Yields refer to those of isolated pure products using 5 mol % catalyst loading. [b]4 mol % catalyst was used.

terms of yield and time were achieved by carrying out the reaction of 4-methoxyphenyl iodide in water at 100 °C in the presence of TBAB for 10 h (Table 1, entry 11). Interestingly, 4-methoxyphenyl bromide remained inert under these conditions. However, optimization of the reaction conditions (Table 2) revealed that selenylation of aryl bromide was successful in PEG-600 at 125 °C for 13 h (Table 2, entry 10). DMF, NMP, DMSO, and DMC are also quite effective for both the reactions. However, H_2O and PEG-600 were chosen for reaction of aryl iodides and bromides, respectively, being more efficient, cost-effective, and environmentally friendly. It is worthwhile to note that two units of PhSe of Ph_2Se_2 are consumed in this reaction.

Thus, in a typical reaction procedure, a mixture of aryl iodide (1 mmol) and diaryl diselenide (0.5 mmol) was heated in water at 100 °C in the presence of Cu-Al_2O_3, KOH, and TBAB for a required period of time (TLC). For aryl bromides, the reaction

Table 2. Standardization of Reaction Conditions for Selenylation of Bromobenzene



entry	solvent	temp (°C)	time (h)	yield[a] (%)
1[b]	H_2O	100	15	
2[b]	H_2O	110	15	
3	toluene	100	15	
4	DMF	140	15	74
5	NMP	140	15	70
6	DMSO	140	15	76
7	DMSO	140	15	76
8	PEG-600	140	15	81
9	PEG-600	125	15	81
10	**PEG-600**	**125**	**13**	**81**
11	PEG-600	125	10	71

[a]Yields refer to those of isolated pure products using 5 mol % catalyst. [b]25 mol % TBAB was used.

was carried out in PEG-600 at 125 °C in the presence of Cu-Al_2O_3 and KOH for a certain period time as required for completion (TLC). Standard workup and purification by column chromatography provided the pure product.

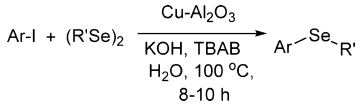
Several diversely substituted aryl and heteroaryl iodides underwent reactions with aryl, heteroaryl, and alkyl diselenides by this procedure to produce the corresponding diaryl, aryl–heteroaryl, and aryl–alkyl selenides. The results are summarized in Table 3.

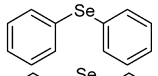
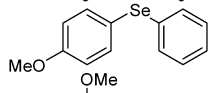
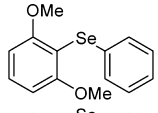
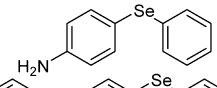
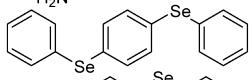
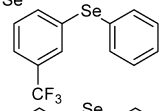
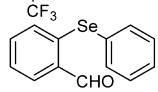
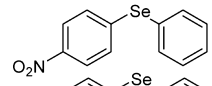
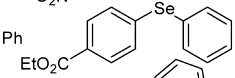
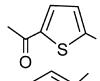
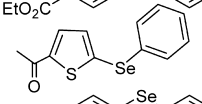
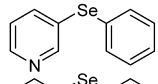
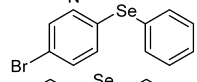
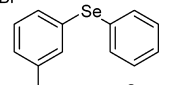
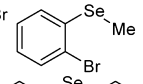
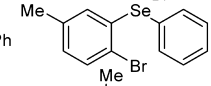
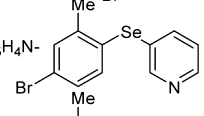
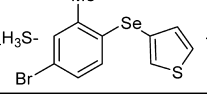
The reaction is highly chemoselective as Br on the phenyl ring of aryl iodides remained inert during coupling with diphenyl diselenide (Table 3, entries 12–17). Several functionalities, such as OMe, NH_2, CF_3, CHO, COMe, NO_2, and CO_2Et, were compatible under the reaction conditions. A sterically hindered molecule, 2,6-dimethoxyiodobenzene, underwent facile selenylation by this procedure (Table 3, entry 3). The heteroaryl iodides containing 5-acetyl-2-thiophenyl and 3-pyridinyl reacted with diphenyl diselenide without any difficulty to provide the corresponding heteroaryl–aryl selenides (Table 3, entries 10 and 11).

A wide range of substituted aryl- and heteroaryl bromides reacted with aryl selenides by the procedure described above (condition B) to furnish the corresponding diaryl and heteroaryl–aryl selenides. The results are reported in Table 4. The naphthyl bromides were equally reactive as phenyl bromides (Table 4, entries 8 and 9) to provide the corresponding selenides by this reaction. These compounds

dx.doi.org/10.1021/jo401062k | J. Org. Chem. 2013, 78, 7145–7153

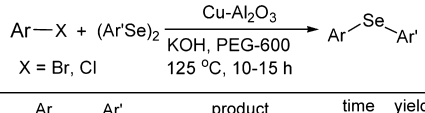
Table 3. Cu-Al_2O_3-Catalyzed Selenylation of Aryl Iodides in Water[a,b]

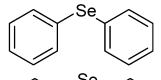
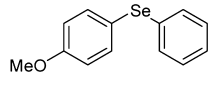
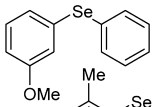
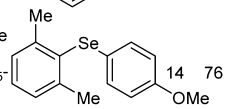
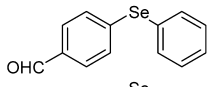
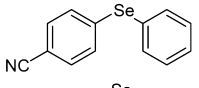
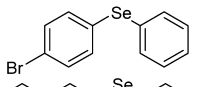
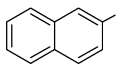
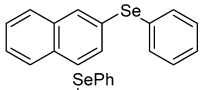
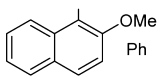
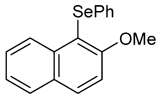
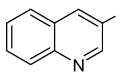
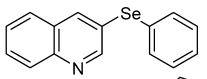
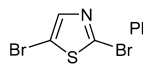
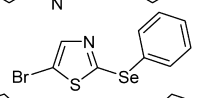
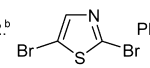
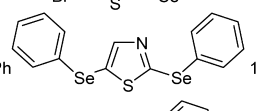
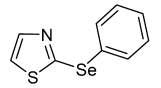


entry	Ar	R'	product	time (h)	yield[a] (%)	ref
1.	C_6H_5-	Ph		9	90	11a
2.	4-OMe-C_6H_4-	Ph		10	84	11a
3.	2, 6-diOMe-C_6H_3-	Ph		10	75	
4.	4-NH_2-C_6H_4-	Ph		10	85	8d
5.[b]	4-I-C_6H_4-	Ph		10	82	8a
6.	3-CF_3-C_6H_4-	Ph		9	88	11a
7.	2-CHO-C_6H_4-	Ph		8	78	11b
8.	4-NO_2-C_6H_4-	Ph		8	95	11a
9.	4-CO_2Et-C_6H_4-	Ph		8	77	8a
10.		Ph		9	89	
11.		Ph		9	90	11b
12.	4-Br-C_6H_4-	Ph		8	91	11c
13.	3-Br-C_6H_4-	Ph		9	88	8d
14.	2-Br-C_6H_4-	Me		8	92	
15.	2-Br-5-Me-C_6H_3-	Ph		10	79	
16.	4-Br-2-Me-C_6H_3-	3-C_5H_4N-		10	83	
17.	4-Br-2-Me-C_6H_3-	3-C_4H_3S-		10	85	

[a]Yields refer to those of isolated pure products. [b]2 equiv (1 mmol) of Ph_2Se_2 was used.

Table 4. Cu-Al_2O_3-Catalyzed Selenylation of Aryl Bromides in PEG-600[a,b]



entry	Ar	Ar'	product	time (h)	yield[a] (%)	ref
1.	C_6H_5-	Ph		12 15	(i) 84 (X = Br) (ii) 25 (X = Cl)	11a
2.	4-OMe-C_6H_4-	Ph		13 15	(i) 81 (X = Br) (ii) 0 (X = Cl)	11a
3.	3-OMe-C_6H_4-	Ph		11	88	8c
4.	2, 6-diMe-C_6H_3-	4-OMe-C_6H_5-		14	76	
5.	4-CHO-C_6H_4-	Ph		11 14	(i) 81 (X = Br) (ii) 54 (X = Cl)	8a
6.	4-CN-C_6H_4-	Ph		10 14	(i) 87 (X = Br) (ii) 55 (X = Cl)	11c
7.	4-Br-C_6H_4-	Ph		11	84	11c
8.		Ph		13	83	8b
9.		Ph		15	84	
10.		Ph		12	81	11b
11.		Ph		11	82	
12.[b]		Ph		11	80	
13.		Ph		12	85	
14.	2, 4-diNO_2-C_6H_3-	Ph	**2**	10	92	12

[a]Yields refer to those of isolated pure products. [b]2 equiv (1 mmol) of Ph_2Se_2 was used.

are of much importance, being analogues of 5-LOX inhibitor **4** (Figure 1). The sterically hindered 2,6-dimethylbromobenzene reacted cleanly with di-4-methoxyphenyl diselenide (Table 4, entry 4). Significantly, 1,4-dibromobenzene underwent exclusive monoselenylation on treatment with diphenyl diselenide (Table 4, entry 7). Several heteroaryl bromides bearing quinolinyl and thiazolyl moieties also underwent smooth reactions (Table 4, entries 10−13). Interestingly, when 1 equiv of diphenyl diselenide was used, 2,5-dibromothiazole provided one product selectively, keeping the 5-Br unaffected (Table 4, entry 11). However, use of 2 equiv of diphenyl diselenide provided the corresponding bis-selenide (Table 4, entry 12). A potent bioactive molecule **2** (Figure 1), the inhibitor of thioredoxin reductase (TR) and glutathione reductase (GR), has been successfully obtained by this reaction (Table 4, entry 14).[8c,12] The aryl chlorides were not very reactive under these reaction conditions. The yields of products

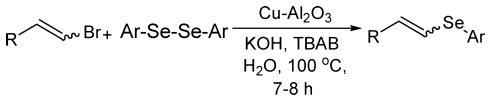
dx.doi.org/10.1021/jo401062k | J. Org. Chem. 2013, 78, 7145−7153

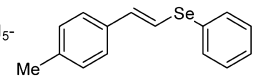
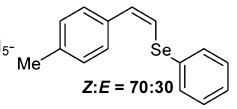
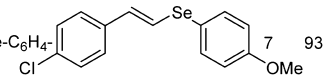
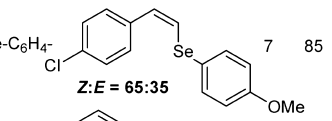
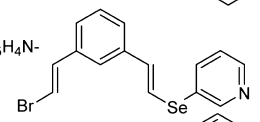
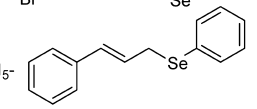
vary with the nature of the substituent on the phenyl ring of aryl chloride.

The electron-withdrawing groups accelerated the reaction to a great extent, pushing the yields to 54−55% (Table 4, entries 5 and 6), whereas the electron-donating group arrested the selenylation completely (Table 4, entry 2). The unsubstituted chlorobenzene, however, underwent the reaction marginally (Table 4, entry 1).

The selenylation of styrenyl bromides proceeded efficiently in water in the presence of TBAB by the same procedure as that for aryl iodides. The results are presented in Table 5. The *trans*-

Table 5. Cu-Al_2O_3-Catalyzed Selenylation of Styryl Bromides in Water[a]



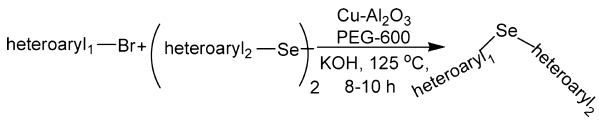
entry	R	Ar	product	time (h)	yield[a] (%)	ref
1.	Me	C_6H_5-		8	90	11a
2.	Me	C_6H_5-	 *Z*:*E* = 70:30	8	83	11a
3.	Cl	4-OMe-C_6H_4-		7	93	
4.	Cl	4-OMe-C_6H_4-	 *Z*:*E* = 65:35	7	85	
5.	Br	3-C_5H_4N-		8	81	
6.		C_6H_5-		7	92	18

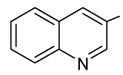
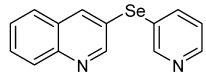
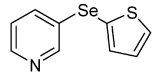
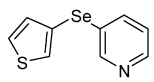
[a]Yields refer to those of isolated pure products.

styrenyl bromides furnished *trans*-selenides (Table 5, entries 1 and 3), whereas *cis*-styrenyl bromides provided mixture of *cis* and *trans* products with *cis* as the major constituent (Table 5, entries 2 and 4), which is not unusual.[11a] Significantly, the bis-vinyl bromide, 1,3-bis((*E*)-2-bromovinyl)benzene on reaction with 3-pyridinyl diselenide produced only monoselenide even when excess diselenide was employed (Table 5, entry 5). The cinnamyl bromide also underwent facile selenylation (Table 5, entry 6).

The reaction of a heteroaryl bromide with a diheteroaryl diselenide proceeded well in PEG-600 under the same conditions as those for aryl bromides. The results are summarized in Table 6. The reactions of quinolinyl, pyridinyl, and thiophenyl bromides with dipyridinyl and dithiophenyl diselenides were performed successfully to provide the corresponding unsymmetrical diheteroaryl selenides for the first time. These selenides might be of much interest for biological activity as the corresponding sulfides are highly potent.[9]

Table 6. Synthesis of Unsymmetrical Heteroaryl−Heteroaryl Selenides[a]



entry	heteroaryl$_1$	heteroaryl$_2$	product	time (h)	yield[a] (%)	ref
1.				8	91	
2.				8	84	
3.				10	81	

[a]Yields refer to those of isolated pure products.

The solvent-controlled selective selenylation of iodo- and bromobenzene prompted us to utilize this property for the synthesis of unsymmetrical bis-selenides, not addressed earlier. Thus, 1,4-bromoiodobenzene was reacted with diphenyl diselenide in water, followed by reaction with dimethyl diselenide in PEG-600, to produce the corresponding unsymmetrical bis-selenide with phenyl and methyl units at two ends (Scheme 2, compound **A**). Similarly, other bis-selenides, 1-(3-(phenylselanyl)phenylselanyl)-4-methoxybenzene (Scheme 2, compound **B**) and 1-(2-(methylselanyl)phenylselanyl)benzene (Scheme 2, compound **C**), were also achieved starting from 1,3-bromoiodo- and 1,2-bromoiodobenzenes. The results are outlined in Scheme 2. The synthesis of these unsymmetrical bis-selenides is reported here for the first time and might be of interest as useful material in analogy to the corresponding bis-sulfide counterparts.[10] Further, an arene bearing two different heterocyclic units connected via a C−Se bond (Scheme 2, compound **D**) is of much significance and may be worthy for biological screening too. This procedure also provides the scope for access to functionalized molecules starting with suitably substituted aryl halides and diselenides.

In general, the reactions are clean and high yielding. The products were obtained pure by a simple workup and chromatography. Many of these selenides were not reported earlier. Several useful functionalities and sensitive heterocyclic moieties are compatible with this procedure.

For recyclability and reuse of the catalyst, after the reaction was over, the reaction mixture was filtered to separate the catalyst. The solid catalyst was then washed with diethyl ether (5 × 3 mL), water (4 × 3 mL), and acetone (3 × 4 mL). The solid was then dried at 100 °C for 8 h for further use. The catalyst was recycled up to a seventh run without appreciable loss of efficiency for the representative reaction of 4-iodoanisole and diphenyldiselenide (Figure 2). The copper loading of the catalyst after the seventh cycle was found to be 0.491 mmol/g compared to 0.515 mmol/g in the fresh catalyst (as detected by ICP-MS).

To investigate the reaction mechanism, a series of experiments were conducted. The X-ray photoelectron spectroscopic (XPS) study of the fresh and used catalysts at the Cu 2p level shows the $2p_{3/2}$ lines at 934.7 and 936.4 eV, respectively, with characteristic shakeup features (Figure 3a,b).[13] This clearly

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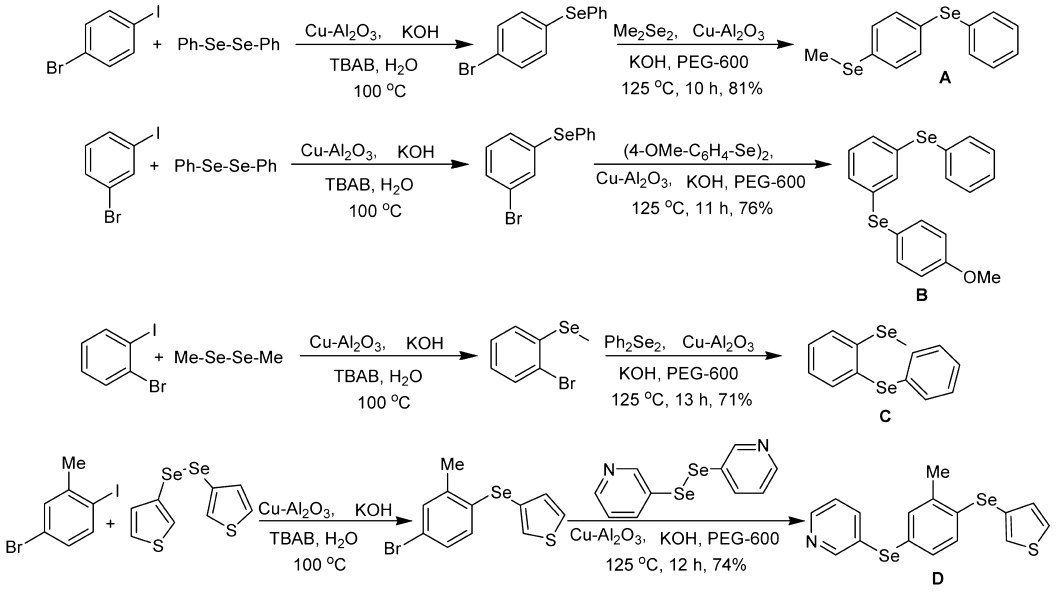
Scheme 2. Solvent-Controlled Differential Selenylation of Bromoiodobenzenes



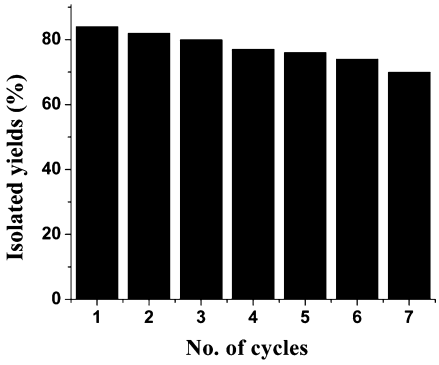


Figure 2. Recyclability of the Cu-Al_2O_3 catalyst.

indicates that Cu is in a +2 oxidation state before and after the reaction (a slightly higher value of binding energy of Cu^{2+} in the used catalyst may be due to the presence of the more electronegative environment of the copper ions in the postreaction phase).

On the other hand, the EPR (electron paramagnetic resonance) spectra of the fresh, intermediate, and the used copper catalysts were recorded for the solid sample at 77 K (Figure 4). The g values of the fresh catalyst are $g_1 = 2.127$, $g_2 = 2.028$ and those of the used catalyst are $g_1 = 2.065$, $g_2 = 2.012$, indicating a tetragonally distorted octahedral geometry for Cu(II).[14] The EPR spectral pattern of the intermediate complex exhibited the g values as $g_1 = 2.058$, $g_2 = 2.034$, and $g_3 = 2.011$, which are indicative of an octahedral environment with a rhombic distortion at the metal center.[11d] From these experiments, it is evident that Cu remains in the +2 oxidation state throughout the reaction cycle. On the other hand, to check the possibility of a single electron transfer (SET) process in the reaction pathway, we chose to use 1-(allyloxy)-2-iodobenzene as a probe in a reaction with diphenyl diselenide following experimental condition A. If the reaction would follow the SET mechanistic process or the radical pathway, then it will end up with the formation of the benzofuran derivative, 2,3-dihydro-3-((phenylselanyl)methyl)benzofuran **E** (Scheme 3).[15] However, we did not observe formation of even

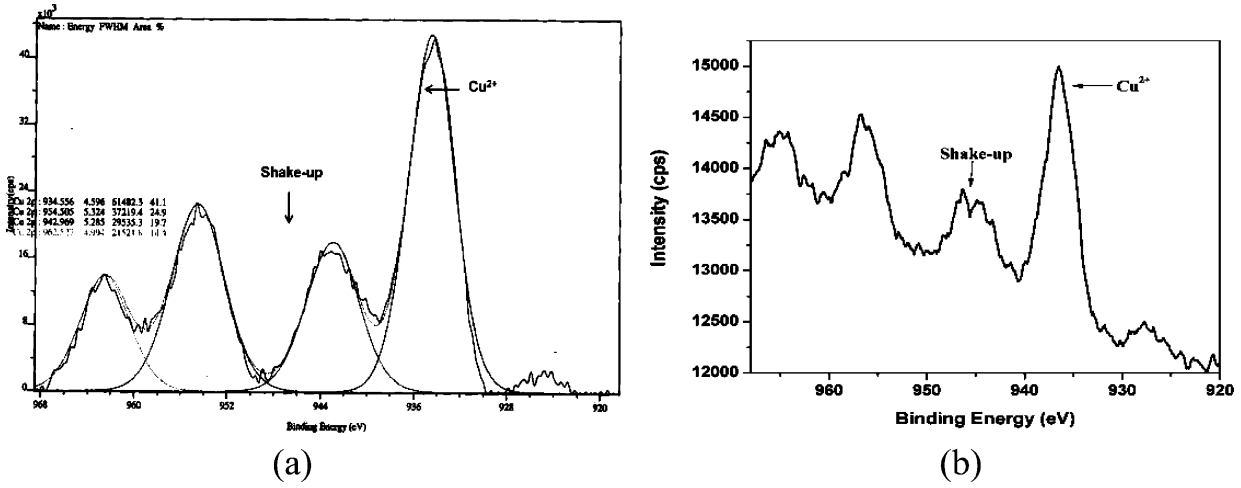


Figure 3. XPS of Cu $2p_{3/2}$ for (a) fresh catalyst and (b) used catalysts.

dx.doi.org/10.1021/jo401062k | J. Org. Chem. 2013, 78, 7145−7153

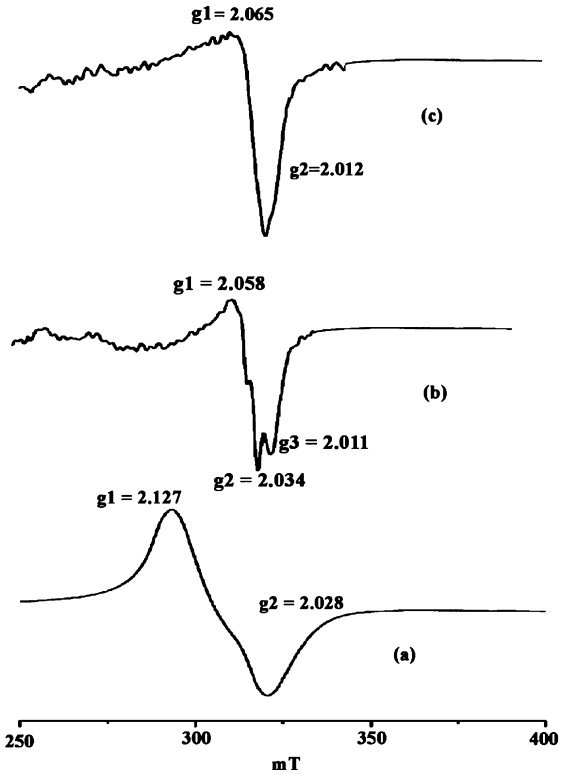
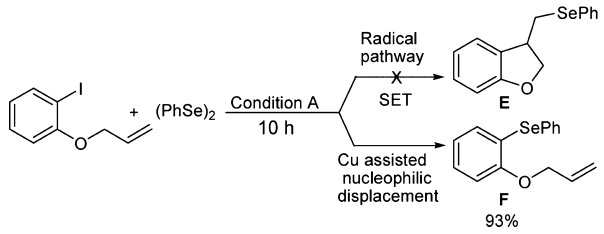


Figure 4. X-band EPR spectral patterns of Cu^{2+} in (a) fresh catalyst, (b) intermediate complex, and (c) used catalyst.

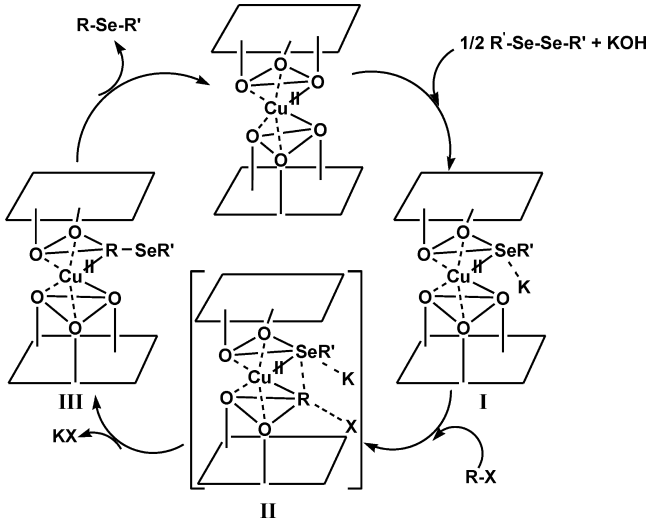
Scheme 3. Selenylation Reaction of 1-(Allyloxy)-2-iodobenzene to Check the SET Process



a trace amount of compound **E** in the crude reaction mixture (NMR), and compound **F**, (2-(allyloxy)phenyl)(phenyl)selane (characterized satisfactorily by ^{1}H NMR, ^{13}C NMR, and elemental analysis), was isolated in 93% yield (Scheme 3). From this experiment, it is not unlikely to conclude that the reaction is not following the SET mechanistic process, and hence, Cu-assisted nucleophilic displacement[16,17] of aryl halide by diaryl diselenide is considered (Scheme 4).

We suggest that, first, KSeR′, generated in situ from R′-Se-Se-R′ and KOH, interacts with the copper catalyst to give an intermediate complex **I** giving rise to a rhombic distortion of the copper(II) coordination geometry. In the next step, RX combines with intermediate **I** to form a transient intermediate **II**, where R interacts with the Se center, being assisted by the Cu(II) species. The intermediate **II** subsequently collapses to intermediate **III** with direct carbon selenium bond formation. Elimination of R-Se-R′ from the coordination sphere of the copper catalyst led to the formation of the product with the regeneration of the catalyst. This type of mechanism was reported earlier too.[11e]

Scheme 4. Plausible Mechanism for Selenylation of Aryl Halide



CONCLUSION

In conclusion, we have developed an efficient protocol for solvent-controlled halo-selective selenylation of aryl iodides and bromides by diaryl diselenides in water and PEG-600, respectively, catalyzed by Cu(II)-Al_2O_3. A library of unsymmetrical aryl−aryl, aryl−alkyl, aryl−heteroaryl, and diheteroaryl mono- and bis-selenides, including a potent bioactive molecule **2**, were easily achieved. The significant advantages of this procedure are simple operation, no need for maintaining an inert atmosphere and using dry solvents, chemoselectivity, high yields, scaling up to multigram quantities, no use of ligands, reaction in an environmentally acceptable medium, easy accessibility, and recyclability of catalyst. To the best of our knowledge, such a solvent-controlled selenylation and the development of an efficient method for the synthesis of unsymmetrical diheteroaryl selenides and organo bis-selenides are reported for the first time. We believe that this will find useful applications in the synthesis of organoselenides.

EXPERIMENTAL SECTION

General. The aryl and heteroaryl diselenides used in this reaction were prepared following a reported procedure.[19] Diphenyl diselenide and dimethyl diselenide were purchased from a chemical supplier. HRMS analysis was performed in a Qtof mass analyzer using the ESI ionization method. Thin-layer chromatography was done using commercial (MERCK) plates with silica gel 60 F_{254}.

General Experimental Procedure for the Cross-Coupling of Aryl Halides and Diaryldiselenides. Representative Procedure for the Reaction of 4-Iodoanisole and Diphenyldiselenide (Table 3, Entry 2). A mixture of 4-iodoanisole (234 mg, 1 mmol), diphenyldiselenide (156 mg, 0.5 mmol), KOH (84 mg, 1.5 mmol), tetrabutylammonium bromide (TBAB) (80 mg, 0.25 mmol), and Cu(II)-Al_2O_3 catalyst (97 mg, 5 mol %) in water (4 mL) was heated with stirring at 100 °C under air for 10 h (TLC). The reaction mixture was filtered to separate the solid catalyst, which was used for successive cycles. The filtrate was extracted with Et_2O (4 × 15 mL). The extract was washed with water and brine and then dried (Na_2SO_4). Evaporation of the solvent left the crude product, which was purified by column chromatography over silica gel (60−120 mesh) (hexane/diethyl ether 95:5) to afford pure (4-methoxyphenyl)(phenyl)selane (221 mg, 84%) as a pale yellow liquid: R_f = 0.7 (hexane/diethyl ether = 9:1); IR (neat) 3064, 2925, 2827, 1577, 1473, 1285 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.86 (d, J = 7 Hz, 2H), 7.18−7.21 (m, 3H), 7.33 (d, J = 7 Hz, 2H), 7.51 (d, J = 7 Hz, 2H); ^{13}C NMR

dx.doi.org/10.1021/jo401062k | J. Org. Chem. 2013, 78, 7145−7153

(125 MHz, $CDCl_3$) δ 55.4, 115.3 (2C), 120.1, 126.6, 129.3 (2C), 131.1 (2C), 133.3, 136.6 (2C), 159.9. The spectroscopic data (^1H and ^{13}C NMR) are in good agreement with those reported for the authentic sample.[11b] This procedure was followed for all the reactions listed in Table 3.

Representative Procedure for the Reaction of 4-Bromoanisole and Diphenyldiselenide (Table 4, Entry 2). The same procedure as that in the previous experiment was followed in PEG-600 (4 mL), replacing water and in the absence of TBAB, allowing the reaction to go for 13 h at 125 °C (TLC). Extraction and workup provided pure (4-methoxyphenyl)(phenyl)selane (213 mg, 81%) as a pale yellow liquid. This procedure was followed for all of the reactions listed in Table 4. Although these procedures were described with a 1 mmol scale, 10 mmol scale reactions also provided uniform results.

All of these products listed in Tables 3 and 4 were properly characterized. The known compounds were identified by comparison of their spectra with those of authentic samples (see references in Tables 3−5). The unknown compounds were characterized by their spectroscopic data (IR, ^1H and ^{13}C NMR, and HRMS or elemental analysis data), which are provided below in order of their entries in the respective tables.

(2,6-Dimethoxyphenyl)(phenyl)selane (Table 3, Entry 3): Yellow solid (220 mg, 75%); mp 75−77 °C; R_f = 0.55 (hexane/diethyl ether = 9:1); IR (KBr) 3060, 2921, 2823, 1597, 1562, 1484, 1391, 1276, 1021 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 6H), 6.62 (d, J = 8 Hz, 2H), 7.09−7.15 (m, 3H), 7.24 (d, J = 8 Hz, 2H), 7.34 (t, J = 8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.4 (2C), 104.5 (2C), 125.6 (2C), 128.7 (2C), 129.7 (2C), 131.1, 132.9, 161.0 (2C). HRMS Calcd for $C_{14}H_{14}O_2Se$ $[M + H]^+$: 295.0234. Found: 295.0232.

1-(5-(Phenylselanyl)thiophen-2-yl)ethanone (Table 3, Entry 10): Pale yellow liquid (250 mg, 89%); R_f = 0.65 (hexane/diethyl ether = 9:1); IR (neat) 3055, 2921, 1734, 1575, 1491, 1476, 1350, 1022, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.19 (d, J = 4 Hz, 1H), 7.29−7.30 (m, 3H), 7.50−7.53 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7, 128.3, 129.7 (2C), 130.7, 132.7 (2C), 132.9, 134.5, 136.8, 148.2, 189.8. Anal. Calcd for $C_{12}H_{10}OSSe$: C, 51.25; H, 3.58. Found: C, 51.28; H, 3.54.

(2-Bromophenyl)(methyl)selane (Table 3, Entry 14): Pale yellow liquid (230 mg, 92%); R_f = 0.8 (hexane/diethyl ether = 9:1); IR (neat) 3051, 2925, 1664, 1635, 1575, 1538, 1475, 1456, 1436, 1375, 1014, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.04 (t, J = 7 Hz, 1H), 7.19- 7.28 (m, 2H), 7.49 (d, J = 8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.3, 124.1, 126.7, 127.9, 128.6, 132.7, 135.2. Anal. Calcd for C_7H_7BrSe: C, 33.63; H, 2.82. Found: C, 33.66; H, 2.78.

(2-Bromo-5-methylphenyl)(phenyl)selane (Table 3, Entry 15): Yellow liquid (257 mg, 79%); R_f = 0.8 (hexane/diethyl ether = 9:1); IR (neat) 3055, 2918, 1660, 1631, 1575, 1558, 1506, 1474, 1456, 1436, 1015, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 3H), 6.77 (s, 1H), 6.84 (d, J = 8 Hz, 1H), 7.37− 7.41 (m, 4H), 7.60- 7.64 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 120.8, 128.7, 128.8, 129.0, 129.9 (2C), 131.7, 132.5, 135.6, 135.8 (2C), 138.0. Anal. Calcd for $C_{13}H_{11}BrSe$: C, 47.88; H, 3.40. Found: C, 47.84; H, 3.46.

3-(4-Bromo-2-methylphenylselanyl)pyridine (Table 3, Entry 16): Pale yellow liquid (271 mg, 83%); R_f = 0.5 (hexane/ethyl acetate = 9:1); IR (neat) 3039, 2920, 1724, 1566, 1461, 1404, 1377, 1195, 1029 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.21 (s, 3H), 7.40 (s, 1H), 7.65 (s, 1H), 8.51 (s, 1H), 8.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 122.6, 124.6, 128.2, 129.3, 130.1, 133.4, 135.7, 140.0, 142.4, 148.3, 152.5. HRMS Calcd for $C_{12}H_{10}BrNSe$ $[M + H]^+$: 327.9232. Found: 327.9233.

3-(4-Bromo-2-methylphenylselanyl)thiophene (Table 3, Entry 17): Colorless liquid (282 mg, 85%); R_f = 0.7 (hexane/diethyl ether = 9:1); IR (neat) 3101, 2921, 1599, 1458, 1377, 1346, 1195, 1089, 1029, 846, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.94 (d, J = 8 Hz, 1H), 7.07 (dd, J_1 = 5 Hz, J_2 = 1 Hz, 1H), 7.12−7.16 (m, 1H), 7.32 (d, J = 2 Hz, 1H), 7.36−7.39 (m, 1H) 7.41−7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 120.7, 121.6, 127.3, 129.7, 130.0, 132.3, 132.4, 132.8 (2C), 140.0. Anal. Calcd for $C_{11}H_9BrSSe$: C, 39.78; H 2.73. Found: C, 39.75; H, 2.76.

(4-Methoxyphenyl)(2,6-dimethylphenyl)selane (Table 4, Entry 4): Colorless oil (221 mg, 76%); R_f = 0.7 (hexane/diethyl ether = 9:1); IR (neat) 3061, 2922, 2831, 1594, 1565, 1481, 1396, 1280, 1136, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 6H), 3.74 (s, 3H), 6.74 (d, J = 9 Hz, 2H), 7.08 (d, J = 9 Hz, 2H), 7.14 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.6 (2C), 55.4, 115.1 (2C), 123.1, 128.0 (2C), 128.9 (2C), 131.1 (2C), 131.6, 143.5, 158.3; Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.81; H, 5.59.

(2-Methoxynaphthalen-1-yl)(phenyl)selane (Table 4, Entry 9): Pale yellow liquid (263 mg, 84%); R_f = 0.6 (hexane/diethyl ether = 9:1); IR (neat) 3396, 3057, 2924, 2841, 1620, 1591, 1575, 1502, 1475, 1265, 1066 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.1 (d, J = 7 Hz, 3H), 7.17 (d, J = 7 Hz, 2H), 7.35−7.38 (m, 2H), 7.48 (t, J = 8 Hz, 1H), 7.80 (d, J = 8 Hz, 1H), 7.95 (d, J = 9 Hz, 1H), 8.47 (d, J = 9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 57.2, 113.6, 124.2, 125.7, 127.7, 127.9, 128.4, 129.0 (2C), 129.4 (2C), 129.8, 132.1, 133.3, 136.5, 136.7, 158.8. Anal. Calcd for $C_{17}H_{14}OSe$: C, 65.18; H, 4.50. Found: C, 65.15; H, 4.48.

5-Bromo-2-(phenylselanyl)thiazole (Table 4, Entry 11): Pale yellow liquid (261 mg, 82%); R_f = 0.6 (hexane/ethyl acetate = 9:1); IR (neat) 3070, 2923, 2850, 1575, 1475, 1438, 1382, 993 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36−7.44 (m, 3H), 7.59 (s, 1H), 7.71 (d, J = 5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.2, 127.4, 129.7, 130.0 (2C), 135.5 (2C), 145.3, 159.2. HRMS Calcd for $C_9H_6BrNSSe$ $[M + H]^+$: 319.8672. Found: 319.8637.

2,5-Bis(phenylselanyl)thiazole (Table 4, Entry 12): Yellow gummy liquid (316 mg, 80%); R_f = 0.6 (hexane/ethyl acetate = 9:1); IR (neat) 3072, 2921, 2865, 1573, 1475, 1425, 1392, 995 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22−7.24 (m, 4H), 7.32−7.34 (m, 2H), 7.37−7.45 (m, 2H), 7.74 (d, J = 5 Hz, 2H), 7.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.6, 127.3, 127.5, 129.5 (2C), 129.9, 130.1 (2C), 130.8 (2C), 131.8, 135.9 (2C), 151.5, 165.0. Anal. Calcd for $C_{15}H_{11}NSSe_2$: C, 45.58; H, 2.81; N, 3.54. Found: C, 45.54; H, 2.85; N, 3.56.

2-(Phenylselanyl)thiazole (Table 4, Entry 13): Pale yellow liquid (204 mg, 85%); R_f = 0.6 (hexane/ethyl acetate = 9:1); IR (neat) 3077, 2938, 2860, 1575, 1473, 1438, 1381, 991 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 4 Hz, 1H), 7.38−7.46 (m, 3H), 7.74 (d, J = 8 Hz, 2H), 7.78 (d, J = 4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.2, 128.2, 129.4, 129.9 (2C), 135.2 (2C), 144.1, 157.8. HRMS Calcd for C_9H_7NSSe $[M + H]^+$: 241.9531. Found: 241.9537.

(*E*)-(4-Chlorostyryl)(4-methoxyphenyl)selane (Table 5, Entry 3): Light yellow solid (300 mg, 93%); mp 79−81 °C; R_f = 0.7 (hexane/diethyl ether = 9:1); IR (KBr) 3078, 2908, 2839, 1589, 1570, 1491, 1400, 1286, 1247, 1176, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 3H), 6.51 (d, J = 16 Hz, 1H), 6.80 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 16 Hz, 1H), 7.10 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 2H) 7.43 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 115.3 (2C), 118.8, 122.5, 127.1 (2C), 128.8 (2C), 131.1, 132.9, 135.8, 136.0 (2C), 160.0. Anal. Calcd for $C_{15}H_{13}ClSe$: C, 58.56; H, 4.26. Found: C, 58.51; H, 4.29.

Mixture of (*Z*)- and (*E*)-(4-Chlorostyryl)(4-methoxyphenyl)selane (*Z*:*E* = 65:35) (Table 5, Entry 4): Pale yellow solid (274 mg, 85%); R_f = 0.7 (hexane/diethyl ether = 9:1); IR (KBr) 3071, 2916, 2839, 1588, 1571, 1491, 1401, 1285, 1147, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.73 (s, 3H), 6.65 (d, J = 10 Hz, 1H), 6.74−6.81 (m, 5H), 7.16−7.20 (m, 4H), 7.22−7.29 (m, 6H), 7.42−7.45 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 55.5, 100.3, 110.2, 115.2 (2C), 115.5 (2C), 118.1, 121.9, 126.8, 127.1, 128.0, 128.6 (2C), 128.7 (2C), 128.9, 129.6 (2C), 132.3 (2C), 132.9 (2C), 134.5, 135.3 (2C), 135.9, 159.7, 159.8.

3-(3-((*E*)-2-Bromovinyl)styrylselanyl)pyridine (Table 5, Entry 5): Yellow oil (295 mg, 81%); R_f = 0.45 (hexane/ethyl acetate = 9:1); IR (neat) 3062, 2925, 2841, 1581, 1563, 1469, 1421, 1271, 1141, 1035 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.80 (d, J = 14 Hz, 1H), 6.96 (d, J = 15.5 Hz, 1H), 7.07−7.13 (m, 2H), 7.21−7.30 (m, 5H), 7.53 (br s, 1H), 8.03 (d, J = 7.5 Hz, 1H), 8.89 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.7, 115.9, 124.4, 125.8, 126.0, 126.4 (2C), 129.2, 129.4,

dx.doi.org/10.1021/jo401062k | J. Org. Chem. 2013, 78, 7145−7153

136.6, 136.7 (2C), 136.9, 139.8, 143.0. HRMS Calcd for $C_{15}H_{12}BrNSe$ $[M + H]^+$: 365.9375. Found: 365.9389.

3-(Pyridin-3-ylselanyl)quinoline (Table 6, Entry 1): Yellow oil (259 mg, 91%); R_f = 0.2 (hexane/ethyl acetate = 9:1); IR (neat) 3446, 3031, 1616, 1558, 1490, 1463, 1404, 1352, 1126, 1012, 948 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18−7.22 (m, 1H), 7.55 (t, J = 8 Hz, 1H), 7.68−7.79 (m, 3H), 8.07 (d, J = 8 Hz, 1H), 8.28 (s, 1H), 8.52 (s, 1H), 8.74 (s, 1H), 8.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.9, 124.7, 127.4, 127.5, 128.6 (2C), 129.5, 130.2, 140.5, 140.6, 147.1, 148.9, 153.0, 153.5. HRMS Calcd for $C_{14}H_{10}N_2Se$ $[M + H]^+$: 287.0078. Found: 287.0083.

3-(Thiophen-2-ylselanyl)pyridine (Table 6, Entry 2): Colorless viscous liquid (201 mg, 84%); R_f = 0.4 (hexane/ethyl acetate = 9:1); IR (neat) 3456, 3029, 1568, 1471, 1458, 1351, 1136, 993 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.05 (t, J = 4 Hz, 1H), 7.16 (m, 1H), 7.35 (d, J = 3 Hz, 1H), 7.48 (d, J = 6 Hz, 1H), 7.63 (d, J = 8 Hz, 1H), 8.42 (s, 1H), 8.59 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.7, 124.4, 128.6, 130.8, 132.7, 137.6, 137.9, 147.9, 150.5. HRMS Calcd for C_9H_7NSSe $[M + H]^+$: 241.9531. Found: 241.9538.

3-(Thiophen-3-ylselanyl)pyridine (Table 6, Entry 3): Colorless liquid (194 mg, 81%); R_f = 0.4 (hexane/ethyl acetate = 9:1); IR (neat) 3455, 3021, 1565, 1472, 1452, 1350, 1132, 990 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, J = 5 Hz, 1H), 7.15−7.19 (m, 1H), 7.36−7.38 (m, 1H), 7.48−7.49 (m, 1H), 7.62−7.66 (m, 1H), 8.43 (d, J = 4 Hz, 1H), 8.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.0, 124.4, 127.5, 130.2, 130.5, 132.7, 138.9, 147.4, 150.7. Anal. Calcd for C_9H_7NSSe: C, 45.01; H, 2.94; N, 5.83. Found: C, 45.05; H, 2.96; N, 5.81.

1-(4-(Methylselanyl)phenylselanyl)benzene (Scheme 2, Compound A): Yellow viscous liquid (264 mg, 81%); R_f = 0.65 (hexane/diethyl ether = 9:1); IR (neat) 3055, 2920, 2850, 1577, 1475, 1437, 1384, 1215, 1097 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.47 (s, 3H), 7.16 (d, J = 8 Hz, 2H), 7.25−7.31 (m, 4H), 7.43 (d, J = 8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.8, 111.7, 126.9, 127.2, 127.4 (2C), 129.4 (2C), 132.5 (2C), 134.2 (2C), 138.6. Anal. Calcd for $C_{13}H_{12}Se_2$: C, 47.87; H, 3.71. Found: C, 47.82; H, 3.74.

1-(3-(Phenylselanyl)phenylselanyl)-4-methoxybenzene (Scheme 2, Compound B): Pale yellow liquid (317 mg, 76%); R_f = 0.55 (hexane/diethyl ether = 9:1); IR (neat) 3057, 2924, 2835, 1591, 1570, 1491, 1438, 1286, 1246, 1172, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.74−6.79 (m, 4H), 7.09−7.18 (m, 4H), 7.26 (t, J = 7 Hz, 2H), 7.33−7.42 (m, 1H), 7.45 (d, J = 8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 115.2, 115.5 (2C), 120.1, 126.6 (2C), 129.2 (2C), 131.0 (2C), 133.3 (2C), 133.6 (2C), 136.6 (2C), 137.2, 159.9. Anal. Calcd for $C_{19}H_{16}OSe_2$: C, 54.56; H, 3.86. Found: C, 54.59; H, 3.82.

1-(2-(Methylselanyl)phenylselanyl)benzene (Scheme 2, Compound C): Yellow oil (231 mg, 71%); R_f = 0.6 (hexane/diethyl ether = 9:1); IR (neat) 3051, 2935, 2831, 1575, 1482, 1430, 1375, 1220, 1095 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 7.00 (d, J = 8 Hz, 1H), 7.07−7.09 (m, 1H), 7.13 (t, J = 7 Hz, 1H), 7.17 (d, J = 8 Hz, 1H), 7.21 (t, J = 3 Hz, 1H), 7.24−7.26 (m, 2H), 7.39−7.41 (m, 1H), 7.45−7.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.1, 127.1, 128.0, 128.1, 129.5 (2C), 129.6, 130.0, 130.5, 133.4 (2C), 133.7, 134.1. Anal. Calcd for $C_{13}H_{12}Se_2$: C, 47.87; H, 3.71. Found: C, 47.89; H, 3.72.

3-(3-Methyl-4-(thiophen-3-ylselanyl)phenylselanyl)pyridine (Scheme 2, Compound D): Pale yellow oil (302 mg, 74%); R_f = 0.5 (hexane/ethyl acetate = 9:1); IR (neat) 3386, 3099, 2921, 1739, 1566, 1461, 1404, 1348, 1193, 1083, 1031, 1012, 846 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.91 (d, J = 8 Hz, 1H), 7.08−7.20 (m, 2H), 7.30 (s, 1H), 7.35−7.39 (m, 2H), 7.45−7.48 (m, 1H), 7.70 (d, J = 12 Hz, 1H), 8.57 (s, 1H), 8.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 121.3, 124.5, 127.2, 127.4, 130.3, 130.8, 131.2, 132.0, 132.8, 133.2, 135.2, 140.1, 148.3, 152.6. Anal. Calcd for $C_{16}H_{13}NSSe_2$: C, 46.96; H, 3.20; N, 3.42. Found: C, 46.91; H, 3.23; N, 3.45.

(2-(Allyloxy)phenyl)(phenyl)selane (Scheme 3, Compound F): White solid (269 mg, 93%); mp 46−48 °C; R_f = 0.75 (hexane/diethyl ether = 9:1); IR (KBr) 3058, 2885, 2858, 1886, 1764, 1645, 1573, 1471, 1440, 1379, 1274, 1240, 1132, 1101, 1018, 997, 921, 774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.61−4.65 (m, 2H), 5.32 (dd, J_1 = 12 Hz, J_2 = 1.5 Hz, 1H), 5.49 (dd, J_1 = 15 Hz, J_2 = 1.5 Hz, 1H), 6.02−6.12 (m, 1H), 6.81−6.89 (m, 2H), 7.02 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.17−7.22 (m, 1H), 7.36−7.40 (m, 3H), 7.64−7.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.3, 111.9, 117.4, 121.8, 122.7, 127.5, 128.1, 128.3, 129.5 (2C), 130.7, 132.9, 135.6 (2C), 155.6. Anal. Calcd for $C_{15}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 62.25; H, 4.90.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The copies of ^1H NMR and ^{13}C NMR spectra of all products listed in Tables 3−6 and in Schemes 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are pleased to acknowledge the financial support from CSIR, New Delhi [Grant no. 01(2365/10/EMR-II], and DST, New Delhi, for a J.C. Bose Fellowship to B.C.R. (Grant no. SR/S2/JCB-11/2008) for this investigation. T.C. thanks CSIR for his fellowship.

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