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Highly efficient and reusable MCM-41-immobilized bipyridine copper(I) catalyst for the C–Se coupling of organoboronic acids with diaryl diselenides

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A highly efficient MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] was prepared from 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bi-pyridine via immobilization on mesoporous material MCM-41, followed by reacting with CuI. In the presence of 5 mol% MCM-41-bpy-CuI, the cross-coupling reaction of organoboronic acids with diaryl diselenides proceeded smoothly in DMSO/H_2O (2/1) at 110 °C under air to afford a variety of diorganyl selenides in good to excellent yields. This heterogeneous copper catalyst can be recovered and recycled by a simple filtration of the reaction solution and used for at least 10 consecutive trials without any decreases in activity.

Introduction

Diorganyl selenides have found widespread utilization as important intermediates or reagents in organic synthesis and many methods for the synthesis of these compounds have been developed.[1] However, in most cases unstable selenium reagents are usually used as selenium sources. Therefore, there is further scope to explore new synthetic methods using stable selenium reagents. Diaryl diselenides are stable selenium

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reagents for preparation of unsymmetrical diorganyl selenides via chemical cleavage of Se–Se bonds in the presence of a reducing agent such as $NaBH_4$, Na/NH_3, Bu_3SnH, $LiAlH_4$, etc.[2] Transition metal-catalyzed cleavage of Se–Se bonds in diaryl diselenides is considered more applicable for preparation of functional unsymmetrical diorganyl selenides[3] since many functional groups cannot withstand the harsh conditions for chemical cleavage of Se–Se bonds. Indium(I) iodide-catalyzed synthesis of unsymmetrical diorganyl selenides was achieved by cleavage of diaryl diselenides and subsequent condensation with alkyl halides or acyl chlorides.[4] $RuCl_3$-catalyzed reaction of dibenzyl or diphenyl diselenides with alkyl halides in the presence of zinc has provided an efficient one-pot route to unsymmetrical diorganyl selenides.[5] Nickel bromide-catalyzed cross-coupling of diaryl diselenides with aryl iodides was realized in the presence of a polymer-supported borohydride.[6] In the presence of a bimetallic [Sn(II)/Cu(II)] system, reactions of reactive bromides such as allyl, propargyl, benzyl, and alkynyl bromides with diorganyl diselenides afforded unsymmetrical diorganyl selenides.[7] Copper(I)-catalyzed reactions of diaryl diselenides with arylbornic acids or reactions of diaryl diselenides with aryl iodides in the presence of magnesium gave unsymmetrical monoselenides.[8] Palladium(0)-catalyzed cleavage of diaryl diselenides was also reported for arylselenation.[9] In addition to diorganyl diselenides, phenyl tributylstannyl selenide ($PhSeSnBu_3$) has also been widely used in organic synthesis because of its stability against air and moisture.[10] Sonoda and Beletskaya groups[11] reported a new synthetic method of diorganyl selenides by palladium-catalyzed cross-coupling reaction of $PhSeSnBu_3$ with aryl and alkyl halides.

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Although transition metal-catalyzed cleavage of Se–Se bonds is highly efficient for preparation of diorganyl selenides, the problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. In addition, homogeneous catalysis might result in unacceptable metallic species contamination of the desired isolated product due to the leaching of the catalyst; this being a very serious problem in industry, especially the pharmaceutical industry. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by a simple filtration of the reaction solution and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[12] From the standpoint of environmentally benign organic synthesis, development of immobilized transition-metal catalysts is challenging and important. In an ideal system, they can be recovered by simple filtration and re-used infinitely, and contamination of products by metal is prevented. So far, supported palladium catalysts have successfully been used in a variety of carbon-carbon or carbon-heteroatom bond formation reactions,[12d,12e,13] however, immobilized copper catalysts for organic transformations have received less attention.[14] To the best of our knowledge, heterogeneous copper-catalyzed C–Se bond formation reaction has not been reported until now.

The discovery of mesoporous material MCM-41 has given an enormous stimulus to research in heterogeneous catalysis and provided a new possible candidate for a solid support for immobilizing homogeneous catalysts.[15] The hexagonally-ordered material

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MCM-41 has large and uniform pore size, ultrahigh surface area, big pore volume and rich silanol groups in the inner walls.[16] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel.[17] To date, some functionalized MCM-41-immobilized palladium or rhodium complexes have been prepared and successfully used in organic reactions.[18] Recently, we reported the first synthesis of 3-(2-aminoethylamino)propyl-functionalized MCM-41-supported copper(I) complex [MCM-41-2N-CuI] and found that it is a highly efficient and recyclable heterogeneous catalyst for the homo- and heterocoupling of terminal alkynes[14e] and *N*-arylation reaction of indoles with aryl halides.[14f] In continuing our efforts to develop greener synthetic pathways for organic transformations, herein we wish to report the synthesis of a novel MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] and its application in the C–Se coupling of organoboronic acids with diaryl diselenides.

Results and discussion

A novel MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] was synthesized starting from 3-aminopropyltriethoxysilane, 4,4'-bis(bromomethyl)-2,2'-bipyridine,[19] mesoporous material MCM-41, and CuI according to Scheme 1. Firstly, the reaction of 3-aminopropyltriethoxysilane with 4,4'-bis(bromomethyl)-2,2'-bipyridine in THF at 50 °C in the presence of triethylamine for 6 h gave 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine (BTESBPY), which reacted with MCM-41 in toluene at 100 °C for 24 h, followed by the silylation with Me_3SiCl in

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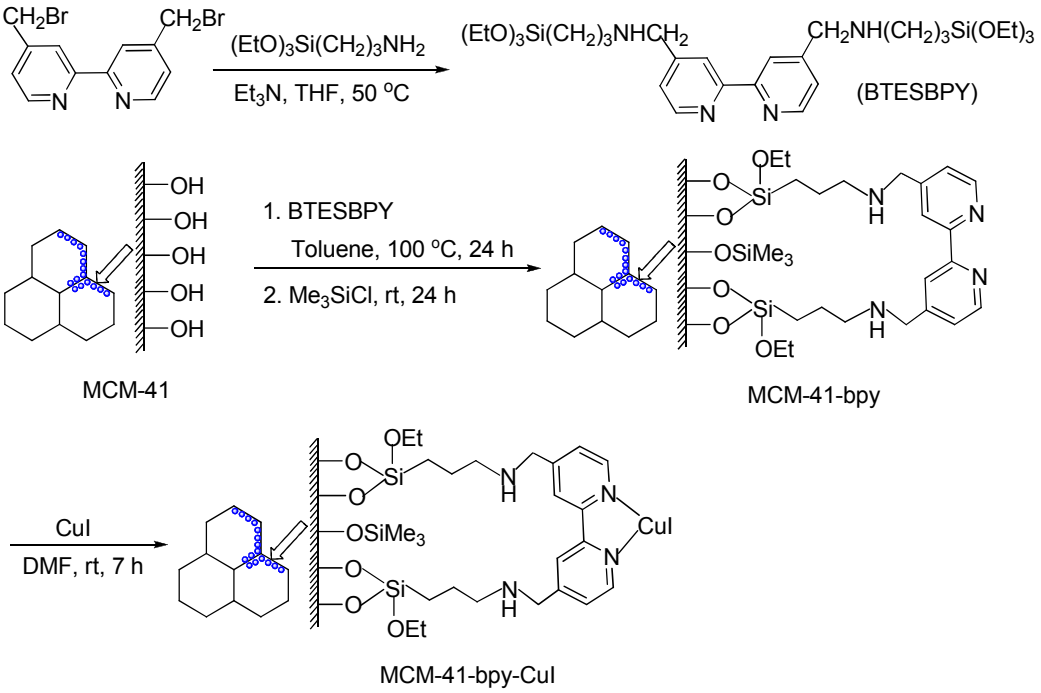
toluene at room temperature for 24 h to generate bipyridine-functionalized MCM-41 (MCM-41-bpy). Then MCM-41-bpy reacted with CuI in DMF at room temperature for 7 h to afford the MCM-41-immobilized bipyridine copper(I) complex catalyst (MCM-41-bpy-CuI) as a pale blue powder, the copper content of the catalyst was found to be 0.63 mmol/g according to the ICP-AES measurements.



Scheme 1. Preparation of MCM-41-bpy-CuI complex

X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-bpy-CuI are displayed in Fig. 1. Small angle X-ray diffraction of MCM-41 gave the peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-bpy-CuI, the (100) reflection of MCM-41 with decreased intensity was remained after functionalization, while the (110) and (200) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework

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and organic moieties which are located inside the channels of MCM-41.

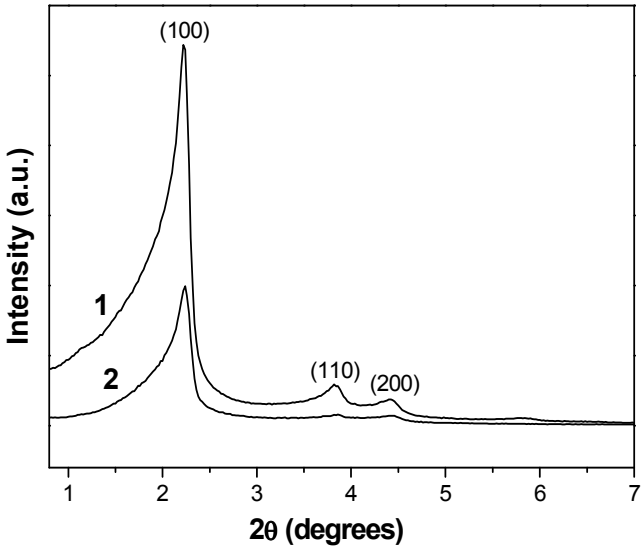

Fig. 1 XRD patterns of the parent MCM-41 (1) and MCM-41-bpy-CuI (2).

The N_2 adsorption-desorption isotherms and pore size distributions for MCM-41 and MCM-41-bpy-CuI are illustrated in Fig. 2 and Fig. 3, respectively. The isotherms in Fig. 2 have remarkable changes before and after grafting as expected because the organic moieties entered the channels, but both samples showed type IV isotherms, characteristic of mesoporous materials according to the IUPAC classification. As shown in Fig. 3, the pore volume and size of MCM-41-bpy-CuI reduced apparently compared with MCM-41, also indicating the organic moieties were introduced into the inner channels, but the pore still remained a narrow distribution. After the grafting the bipyridine copper complex onto MCM-41, the surface area and pore diameter decreased from 902 m^2/g and 2.7 nm to 658 m^2/g and 2.2 nm, respectively, indicating

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that the ordered mesostructure of the parent MCM-41 remained almost intact.

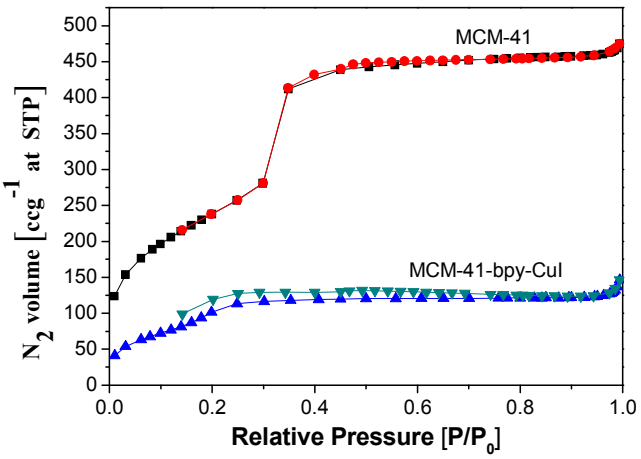

Fig. 2 N_2 adsorption/desorption isotherms of MCM-41 and MCM-41-bpy-CuI

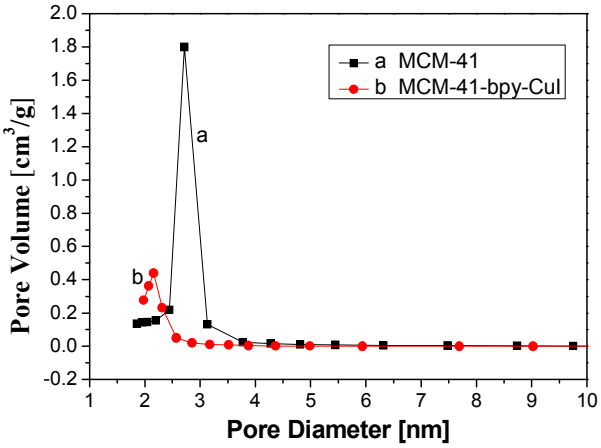

Fig. 3 Pore size distributions of MCM-41 and MCM-41-bpy-CuI

FTIR spectra of MCM-41-bpy and MCM-41-bpy-CuI are presented in Fig. 4. The band observed at 1626 cm^{-1} for MCM-41-bpy could be attributed to the C=N stretching frequency, while the C=N stretching frequency for MCM-41-bpy-CuI is red

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shifted by 12 cm^{-1} and appears at 1614 cm^{-1}. The lowering in frequencies of the C=N peak is indicative of the formation of metal-ligand bond. The thermal stability of organic moieties within the mesoporous material was determined by thermogravi-metric analysis (Fig. 5). As shown in Fig. 5, the parent MCM-41 exhibited excellent thermal stability, no weight loss was observed even at 500 ºC. However, the removal of organocopper complex in MCM-41-bpy-CuI commenced at 240 ºC and continued up to 480 ºC. High resolution transmission electron micrographs (HRTEM) of MCM-41-bpy-CuI are shown in Fig. 6 in the perpendicular direction of the pore axis. The 2D-hexagonal arrangement of the pores with a different contrast than that of the pore walls throughout the specimen is quite clear. Hexagonal pore ordering after the bipyridine grafting and also for Cu(I)-binding with the composite has been observed. It is further confirmed by the respective SAED (selected-area electron diffraction) pattern (Fig. 6, inset) corroborating with the hexagonal ordering of the pores. From XRD data, N_2 adsorption-desorption isotherms, FTIR spectra, TGA data and the TEM images, it can be concluded that the bipyridine copper complex has been successfully grafted onto MCM-41 and the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation. Considering the fact that the MCM-41 support has an extremely high surface area and large pore size, and the catalytic copper species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-supported copper catalyst will exhibit high activity and good reusability.

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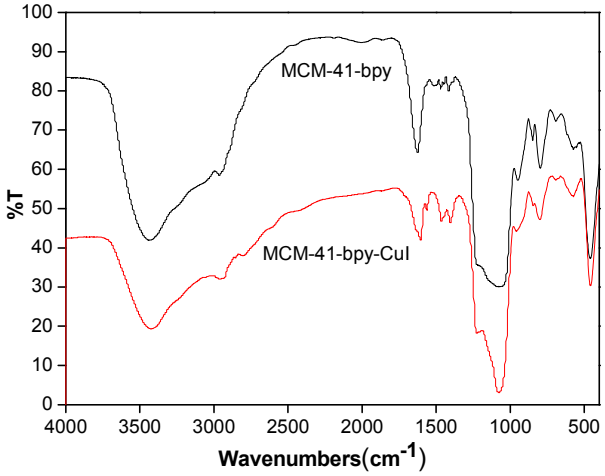

Fig. 4 FTIR spectra of MCM-41-bpy and MCM-41-bpy-CuI

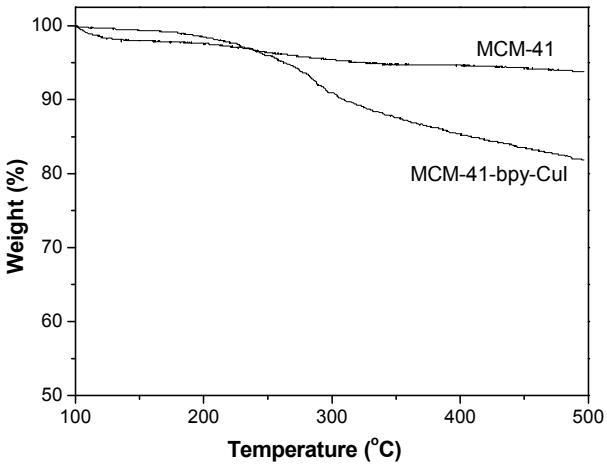

Fig. 5 TGA curves of MCM-41 and MCM-41-bpy-CuI

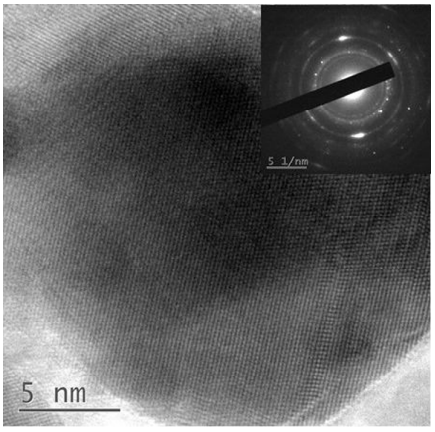

Fig. 6 HRTEM images of MCM-41-bpy-CuI in the direction of the pore axis.

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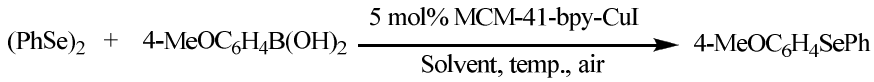
Table 1 Optimization of reaction conditions for the coupling of diphenyl diselenide with 4-methoxyphenylboronic acid[a]



Entry	Solvent (*V/V*)	Temp. (°C)	Time (h)	Yield[b] (%)
1	Toluene	100	24	41
2	DMF	100	24	63
3	DMSO	100	24	79
4	Dioxane	100	24	58
5	DMF/H_2O (2/1)	100	20	85
6	DMSO/H_2O (2/1)	100	18	91
7	Dioxane/H_2O (2/1)	100	24	81
8	DMSO/H_2O (2/1)	110	14	96
9	DMSO/H_2O (2/1)	120	14	95
10[c]	DMSO/H_2O (2/1)	110	8	95
11[d]	DMSO/H_2O (2/1)	110	30	83

[a] Reaction conditions: $(PhSe)_2$ (0.2 mmol), 4-$MeOC_6H_4B(OH)_2$ (0.6 mmol), MCM-41-bpy-CuI (5 mol%), solvent (0.6 mL) under air. [b] Isolated yields. [c] 10 mol% catalyst was used. [d] 2 mol% catalyst was used.

As shown in Table 1, our initial goal was to optimize the reaction conditions for the coupling of diphenyl diselenide (1.0 equiv) and 4-methoxyphenylboronic acid (1.5 equiv) in the presence of 5 mol% Cu (as in MCM-41-bpy-CuI). When the reaction was conducted in common organic solvents such as toluene, DMF, DMSO and dioxane, moderate to good yields were obtained and DMSO was found to be the best choice (Table 1, entries 1-4). To our delight, when a mixture of organic solvent and water (*V/V* = 2/1) was used as the solvent, the yield was improved effectively and the

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DMSO/H_2O (2/1) gave the best result (Table 1, entries 5-7). Our next studies focused on the effect of reaction temperature on the model reaction. For temperatures evaluated [100, 110 and 120 °C], 110 °C was found to be the most efficient and the desired product was isolated in 96% yield (Table 1, entry 8). Reducing the amount of the catalyst resulted in a decrease in yield (Table 1, entry 11). Increasing the amount of the catalyst could shorten the reaction time, but did not improve the yield of desired product (Table 1, entry 10). Thus, the optimized conditions for this transformation are the MCM-41-bpy-CuI (5 mol%) in DMSO/H_2O (2/1) as solvent at 110 °C under air for 14 h (Table 1, entry 8).

With this promising result in hand, we started to investigate the scope of this coupling reaction under the optimized conditions. The scope of both diaryl diselenides and organoboronic acids was explored, and the results are summarized in Table 2. As shown in Table 2, the coupling reactions of diphenyl diselenide **1a** with a variety of arylboronic acids **2a-j** proceeded smoothly under the optimized conditions affording the corresponding diorganyl selenides **3a-3j** in high to excellent yields (Table 2, entries 1-10). The reactions of sterically hindered arylboronic acids such as 2-methyl-phenylboronic acid **2k** and 2-methoxyphenylboronic acid **2l** with **1a** also proceeded smoothly to give the desired products **3k** and **3l** in high yields, respectively (Table 2, entries 11 and 12). The reaction of bulky 1-naphthylboronic acid **2m** gave the corresponding product **3m** in 92% yield (Table 2, entry 13). Heteroarylboronic acids such as 4-pyridylboronic acid **2n**, 6-(dimethylamino)-3-pyridylboronic acid **2o** and 3-thienylboronic acid **2p** could be coupled effectively with **1a** to afford the

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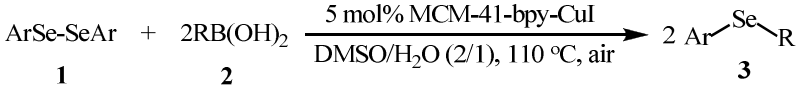
corresponding products **3n-3p** in good to excellent yields (Table 2, entries 14-16). The reaction of (*E*)-styrylboronic acid **2q** with **1a** generated the desired phenyl (*E*)-styryl selenide **3q** in 91% yield (Table 2, entry 17). Generally, the electronic natures of the substituent on the arylboronic acids have limited influence on this heterogeneous copper-catalyzed coupling reaction and various electron-donating and electron-withdrawing substituents such as methoxy, methyl, chloro, fluoro, cyano, ester and dimethylamino were well tolerated. The optimized reaction conditions were also applied to the coupling reactions of substituted diphenyl diselenides such as di(4-methylphenyl) diselenide **1b** and di(4-chlorophenyl) diselenide **1c** with a variety of organoboronic acids, the results are also summarized in Table 2. As shown in Table 2, the reactions of substituted diphenyl diselenides **1b** and **1c** with a variety of organo-boronic acids also proceeded smoothly to give the corresponding diorganyl selenides **3r-3z** in good to excellent yields (entries 18-26). The method provides a quite general route for the synthesis of diorganyl selenides having various functionalities. The results above prompted us to investigate the reaction of diphenyl diselenide **1a** with alkylboronic acids such as methylboronic acd or butylboronic acid. Unfortunately, alkylboronic acids are not reactive under the optimized reaction conditions and no desired product was obtained.

Table 2 Cross-coupling of diaryl diselenides with organoboronic acids catalyzed by MCM-41-bpy-CuI.[a]



Entry	Diaryl diselenide	Organoboronic acid	Product	Yield (%)[b]

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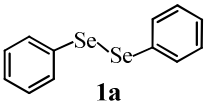
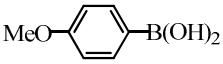
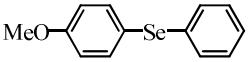
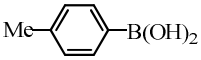
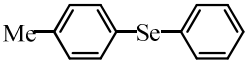
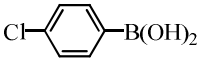
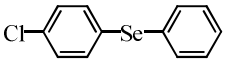
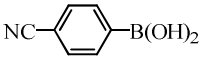
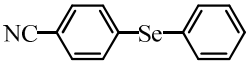
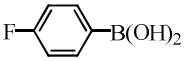
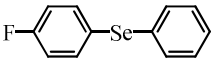
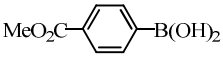
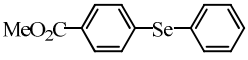
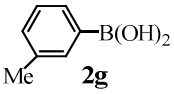
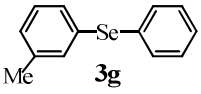
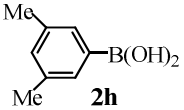
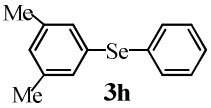
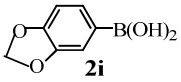
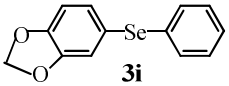
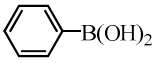
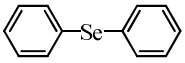
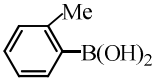
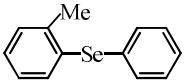
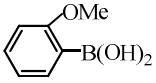
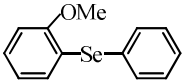
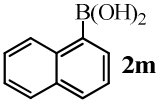
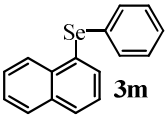
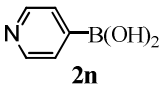
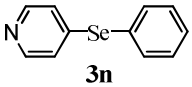
1	 **1a**	 **2a**	 **3a**	96
2	**1a**	 **2b**	 **3b**	92
3	**1a**	 **2c**	 **3c**	93
4	**1a**	 **2d**	 **3d**	91
5	**1a**	 **2e**	 **3e**	89
6	**1a**	 **2f**	 **3f**	88
7	**1a**	 **2g**	 **3g**	91
8	**1a**	 **2h**	 **3h**	92
9	**1a**	 **2i**	 **3i**	98
10	**1a**	 **2j**	 **3j**	87
11	**1a**	 **2k**	 **3k**	90
12	**1a**	 **2l**	 **3l**	89
13	**1a**	 **2m**	 **3m**	92
14	**1a**	 **2n**	 **3n**	91

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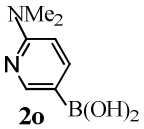
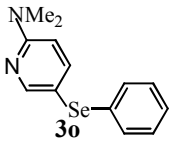
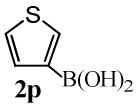
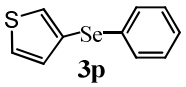
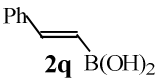
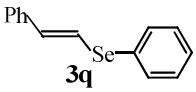
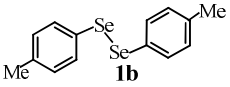
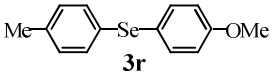
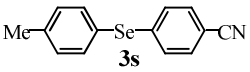
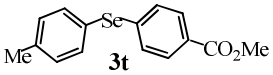
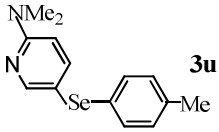
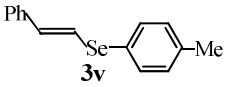
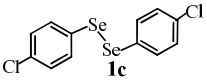
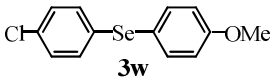
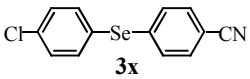
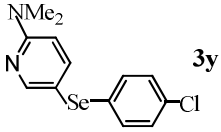
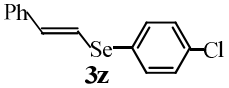
15	**1a**	 **2o**	 **3o**	83
16	**1a**	 **2p**	 **3p**	90
17	**1a**	 **2q**	 **3q**	91
18	 **1b**	**2a**	 **3r**	92
19	**1b**	**2d**	 **3s**	89
20	**1b**	**2f**	 **3t**	91
21	**1b**	**2o**	 **3u**	80
22	**1b**	**2q**	 **3v**	90
23	 **1c**	**2a**	 **3w**	91
24	**1c**	**2d**	 **3x**	90
25	**1c**	**2o**	 **3y**	81
26	**1c**	**2q**	 **3z**	92

[a] Reaction conditions: $(ArSe)_2$ (0.2 mmol), $RB(OH)_2$ (0.6 mmol), MCM-41-bpy-CuI (5 mol%), DMSO (0.4 mL), H_2O (0.2 mL), 110 °C under air for 14 h. [b] Isolated yields.

To determine whether the observed catalysis was due to the heterogeneous catalyst

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MCM-41-bpy-CuI or to a leached copper species in solution, we performed the hot filtration test.[20] We focused on the coupling reaction of diphenyl diselenide with 4-methoxyphenylboronic acid. We filtered off the MCM-41-bpy-CuI complex after 5 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (110 °C) in order to avoid possible recoordination or precipitation of soluble copper upon cooling. We found that, after this hot filtration, no further reaction was observed, indicating that leached copper species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no copper could be detected in the hot filtered solution. This result suggests that the copper catalyst remains on the support at elevated temperature during the reaction and points to a process of heterogeneous nature. This heterogeneous copper(I)-catalyzed coupling reaction of organoboronic acids with diaryl diselenides may proceed through a mechanism analogous to that proposed for the CuI/bpy catalytic system(Scheme 2).[8a] First, the reaction of $RB(OH)_2$ (**2**) with the MCM-41-bpy-CuI affords an MCM-41-immobilized bipyridine Cu^I–R intermediate (**A**), which is coupled with $(ArSe)_2$ (**1**) to give the coupling product ArSeR (**3**) and an MCM-41-immobilized bipyridine Cu^I–SeAr intermediate (**B**). The latter is oxidized by O_2 to form an MCM-41-immobilized bipyridine Cu^{II} intermediate (**C**), which then undergoes a ligand exchange reaction with $RB(OH)_2$ (**2**) to afford an MCM-41-immobilized bipyridine Cu^{II} intermediate (**D**). Finally, the coupling product ArSeR (**3**) is produced again through the oxidation of the intermediate (**D**) and the MCM-41-bpy-CuI is regenerated.

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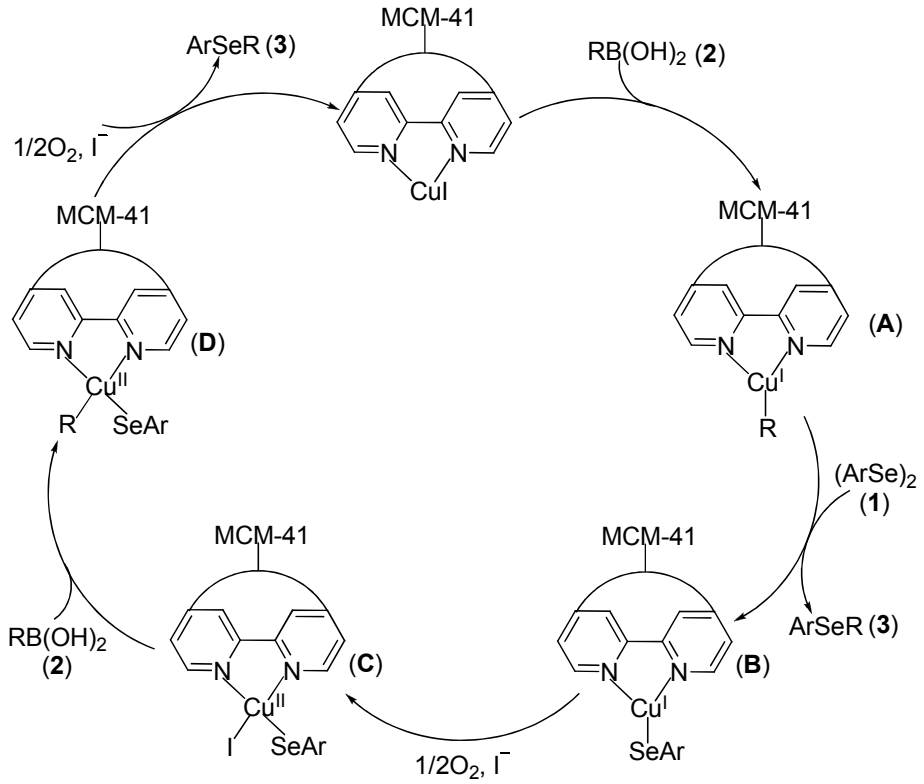

Scheme 2. Plausible reaction mechanism.

For a heterogeneous transition-metal catalyst, it is important to evaluate its ease of separation, recoverability and reusability. We next investigated the recyclability of the MCM-41-bpy-CuI by using the coupling reaction of 4-methoxyphenylboronic acid with diphenyl diselenide. After carrying out the reaction, the catalyst was separated by simple filtration and washed with DMSO, ethanol and diethyl ether. After being air-dried, it can be reused directly without further purification. The recovered copper catalyst was used in the next run, and the average yield of desired **3a** was 95% for 10 consecutive cycles (Table 3, entries 1-10). The high stability and excellent reusability of the catalyst should result from the chelating action of bidentate bipyridine ligand

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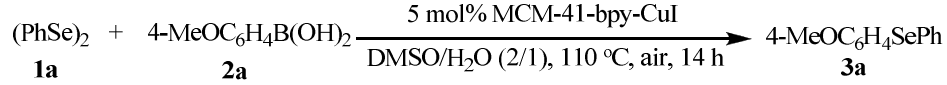
on copper and the mesoporous structure of the MCM-41 support. The result is important from industrial and environmental points of view. The high catalytic activity, excellent reusability and the accessibility of the MCM-41-bpy-CuI complex make it a highly attractive heterogeneous copper catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

Table 3 Coupling reaction of 4-methoxyphenylboronic acid with diphenyl diselenide catalyzed by the recycled catalyst[a]



Cycle	Yield (%)[b]	Cycle	Yield (%)[b]
1	96	2	96
3	95	4	95
5	94	6	95
7	94	8	94
9	93	10	94

[a] Reaction was carried out with **1a** (0.2 mmol), **2a** (0.6 mmol), MCM-41-bpy-CuI (5 mol%), DMSO (0.4 mL), H_2O (0.2 mL), 110 °C under air for 14 h. [b] Isolated yield.

Conclusion

In summary, we have successfully developed a novel, practical and environmentally friendly method for the synthesis of diorganyl selenides through the coupling reaction of diaryl diselenides with organoboronic acids by using an MCM-41-immobilized bipyridine copper(I) complex [MCM-41-bpy-CuI] as catalyst under mild reaction conditions. The reactions generated a variety of diorganyl selenides in good to excellent yields and were applicable to a wide range of organoboronic acids and

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various diaryl diselenides. In addition, this methodology offers the competitiveness of recyclability of the catalyst without loss of catalytic activity, and the catalyst could be easily recovered and reused for at least 10 cycles, thus making this procedure environmentally more acceptable.

Experimental

General comments

All chemicals were reagent grade and used as purchased. All solvents were distilled before use. The products were purified by flash chromatography on silica gel. A mixture of light petroleum ether (30-60 °C) and diethyl ether was generally used as eluent. All products were characterized by comparison of their spectra and physical data with authentic samples. FTIR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ or C_6D_6 as solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in $CDCl_3$ or C_6D_6 as solvent. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. Powder X-ray diffraction patterns were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu-Kα radiation. Nitrogen adsorption/desorption isotherms were obtained using a Bel Japan Inc. Belsorp-HP at 77 K. Prior to gas adsorption measurements materials were degassed for 6 h at 423 K. Thermogravimetric analysis

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(TGA) was performed on a Netzch Sta 449c thermal analyzer system at a heating rate of 10 °C min^{-1} in nitrogen. TEM images were recorded in a Jeol JEM 2010 transmission electron microscope operated at an accelerated voltage of 200 kV. 4,4'-Bis(bromomethyl)-2,2'-bipyridine[19] and mesoporous material MCM-41[21] were prepared according to literature methods.

Preparation of 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine (BTESBPY)

Et_3N (1.52 g, 15 mmol) and 3-aminopropyltriethoxysilane (3.32 g, 15 mmol) were added to a solution of 4,4'-bis(bromomethyl)-2,2'-bipyridine (0.513 g, 1.5 mmol) in THF (10 mL), and the mixture was stirred at 50 °C under Ar for 6 h. After cooling the solution to room temperature, hexane (30 mL) was added and the mixture was filtered through a short $MgSO_4$ column to remove the ammonium salt. The clear solution was then concentrated and dried under vacuum at 100 °C for 24 h to produce the title compound as a pale yellow viscous oil in 92% yield. ^{1}H NMR (400 MHz, C_6D_6) δ (ppm): 8.78 (s, 2H), 8.57 (d, J = 4.2 Hz, 2H), 7.08 (d, J = 4.2 Hz, 2H), 3.76 (q, J = 7.0 Hz, 12H), 3.51 (s, 4H), 2.42 (t, J = 7.0 Hz, 4H), 1.68-1.62 (m, 4H), 1.14 (t, J = 7.0 Hz, 18H), 0.74-0.68 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6) δ (ppm): 156.8, 151.3, 149.3, 123.2, 120.7, 58.5, 53.1, 52.4, 23.9, 18.6, 8.4. Anal. Calcd. for $C_{30}H_{54}N_4O_6Si_2$: C, 57.86; H, 8.74; N, 8.99. Found: C, 57.63; H, 8.52; N, 8.78.

Preparation of MCM-41-bpy

A solution of 2.368 g of 4,4'-bis[3-(triethoxysilyl)propylaminomethyl]-2,2'-bipyridine

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(BTESBPY) in 18 mL of dry chloroform was added to a suspension of 1.881 g of the MCM-41 in 180 mL of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl in 100 mL of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 120 °C for 5 h to obtain 2.963 g of hybrid material MCM-41-bpy. The nitrogen content was found to be 2.91 mmol/g by elemental analysis.

Preparation of MCM-41-bpy-CuI complex

In a small Schlenk tube, 1.00 g of the above-functionalized MCM-41 (MCM-41-bpy) was mixed with 0.15 g (0.78 mmol) of CuI in 10 mL of dry DMF. The mixture was stirred at room temperature for 7 h under an argon atmosphere. The solid product was filtered by suction, washed with DMF and acetone and dried at 40 °C/26.7 Pa under Ar for 5 h to give 1.069 g of a pale blue copper complex (MCM-41-bpy-CuI). The nitrogen and copper contents were found to be 2.67 mmol/g and 0.63 mmol/g, respectively.

General procedure for heterogeneous copper-catalyzed coupling reaction of diaryl diselenides with organoboronic acids

Under an air atmosphere, a Schlenk tube was charged with MCM-41-bpy-CuI (16 mg, 0.01 mmol), diaryl diselenide (0.2 mmol), organoboronic acid (0.6 mmol), DMSO

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(0.4 mL) and H_2O (0.2 mL). The mixture was stirred at 110 °C for 14 h. After completion of the reaction, the reaction mixture was cooled to room temperature, extracted with ethyl acetate (3 × 5 mL), and filtered. The MCM-41-bpy-CuI complex was washed with DMSO (2 × 5 mL), ethanol (2 × 5 mL), and Et_2O (2 × 5 mL) and reused in the next run. The extract was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate = 50:1 to 10:1) to provide the desired product.

4-Methoxyphenyl phenyl selenide 3a. Oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 (d, J = 8.8 Hz, 2H), 7.38-7.33 (m, 2H), 7.25-7.21 (m, 3H), 6.89 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.8, 136.6, 133.3, 130.9, 129.2, 126.5, 119.9, 115.2, 55.3.

4-Methylphenyl phenyl selenide 3b. Oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43-7.40 (m, 4H), 7.25-7.23 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.7, 133.9, 132.2, 132.1, 130.2, 129.3, 126.9, 126.8, 21.2.

4-Chlorophenyl phenyl selenide 3c. Oil.[8a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51-7.48 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.34-7.25 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.1, 133.5, 133.2, 130.7, 129.6, 129.5, 127.7.

4-Cyanophenyl phenyl selenide 3d. Oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62-7.59 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.43-7.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.0, 135.7, 132.4, 130.2, 130.0, 129.2, 127.5, 118.8, 109.6.

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4-Fluorophenyl phenyl selenide 3e. Oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54-7.49 (m, 2H), 7.45-7.42 (m, 2H), 7.30-7.27 (m, 3H), 7.02 (t, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.6 (d, $^1J_{C\text{-}F}$ = 246.0 Hz), 135.8 (d, $^3J_{C\text{-}F}$ = 6.5 Hz), 132.2, 131.7, 129.4, 127.2, 125.2 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 116.6 (d, $^2J_{C\text{-}F}$ = 21.2 Hz).

4-Methoxycarbonylphenyl phenyl selenide 3f. Oil.[8a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.39-7.34 (m, 5H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.8, 139.7, 135.0, 130.4, 130.2, 129.7, 128.7, 128.5, 128.2, 52.2.

3-Methylphenyl phenyl selenide 3g. Oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-7.43 (m, 2H), 7.32-7.25 (m, 5H), 7.16 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.2, 133.8, 132.8, 131.4, 130.7, 130.3, 129.3, 129.2, 128.3, 127.2, 21.3.

3,5-Dimethylphenyl phenyl selenide 3h. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46-7.42 (m, 2H), 7.27-7.24 (m, 3H), 7.12 (s, 2H), 6.91 (s, 1H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.0, 132.6, 131.7, 131.1, 130.3, 129.4, 129.3, 127.1, 21.2. Anal. Calcd. for $C_{14}H_{14}Se$: C, 64.36; H, 5.40. Found: C, 64.08; H, 5.21.

3,4-Methylenedioxyphenyl phenyl selenide 3i. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.39 (m, 2H), 7.28-7.23 (m, 3H), 7.12-7.10 (m, 1H), 7.04 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.4, 147.9, 132.7, 131.5, 129.3, 128.6, 126.8, 121.4, 115.0, 109.3, 101.3. Anal. Calcd. for $C_{13}H_{10}O_2Se$: C, 56.32; H, 3.64. Found: C, 56.45; H, 3.42.

Diphenyl selenide 3j. Oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48-7.45 (m, 4H),

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7.27-7.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 133.0, 131.2, 129.4, 127.4.

2-Methylphenyl phenyl selenide 3k. Oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41-7.38 (m, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.28-7.18 (m, 5H), 7.07 (t, J = 7.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.9, 133.7, 132.8, 131.8, 130.8, 130.3, 129.4, 127.8, 127.2, 126.8, 22.4.

2-Methoxyphenyl phenyl selenide 3l. Oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61-7.58 (m, 2H), 7.36-7.32 (m, 3H), 7.19 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.7, 135.5, 130.9, 129.5, 128.3, 128.1, 127.8, 121.9, 121.7, 110.5, 55.9.

1-Naphthyl phenyl selenide 3m. Oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34-8.31 (m, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 7.2 Hz, 1H), 7.53-7.20 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 134.2, 134.1, 133.9, 131.8, 129.4, 129.3, 129.2, 129.1, 128.6, 127.7, 127.0, 126.9, 126.4, 126.0.

Phenyl 4-pyridyl selenide 3n. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (d, J = 6.0 Hz, 2H), 7.65-7.63 (m, 2H), 7.47-7.38 (m, 3H), 7.10 (d, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.5, 145.8, 136.3, 130.0, 129.4, 126.2, 123.9. Anal. Calcd. for $C_{11}H_9NSe$: C, 56.42; H, 3.87; N, 5.98. Found: C, 56.25; H, 3.59; N, 5.77.

(6-Dimethylamino-3-pyridyl) phenyl selenide 3o. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.38 (d, J = 1.6 Hz, 1H), 7.65 (dd, J = 8.8, 2.4 Hz, 1H), 7.27-7.17 (m, 5H), 6.48 (d, J = 8.8 Hz, 1H), 3.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.8,

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154.7, 144.7, 133.8, 129.8, 129.1, 126.1, 110.4, 106.7, 38.1. Anal. Calcd. for $C_{13}H_{14}N_2Se$: C, 56.32; H, 5.09; N, 10.10. Found: C, 56.17; H, 4.86; N, 9.89.

Phenyl 3-thienyl selenide 3p. Oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 (s, 1H), 7.39-7.35 (m, 3H), 7.28-7.13 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 132.8, 132.3, 131.0, 129.3, 129.2, 126.8, 126.7, 122.7.

Phenyl (*E*)-styryl selenide 3q. Oil.[8a] ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56-7.53 (m, 2H), 7.32-7.23 (m, 8H), 7.18 (d, J = 15.6 Hz, 1H), 6.87 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.1, 135.2, 132.6, 130.2, 129.4, 128.7, 127.7, 127.5, 126.1, 119.5.

4-Methoxyphenyl 4-methylphenyl selenide 3r. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 7.6 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 3.72 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.6, 136.7, 135.8, 131.9, 130.0, 126.8, 120.9, 115.1, 55.3, 21.1. Anal. Calcd. for $C_{14}H_{14}OSe$: C, 60.65; H, 5.09. Found: C, 60.37; H, 5.23.

4-Cyanophenyl 4-methylphenyl selenide 3s. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.8, 139.6, 136.1, 132.3, 130.8, 129.6, 123.5, 118.9, 109.2, 21.3. Anal. Calcd. for $C_{14}H_{11}NSe$: C, 61.77; H, 4.07; N, 5.15. Found: C, 61.49; H, 4.21; N, 5.28.

4-Methoxycarbonylphenyl 4-methylphenyl selenide 3t. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 3.88 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

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δ (ppm): 166.9, 140.7, 138.9, 135.5, 130.5, 129.7, 129.5, 127.8, 124.5, 52.2, 21.3. Anal. Calcd. for $C_{15}H_{14}O_2Se$: C, 59.02; H, 4.62. Found: C, 58.77; H, 4.46.

(6-Dimethylamino-3-pyridyl) 4-methylphenyl selenide 3u. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.37 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 7.02 (d, J = 7.6 Hz, 2H), 6.46 (d, J = 8.8 Hz, 1H), 3.10 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.7, 154.0, 144.5, 144.3, 136.2, 130.6, 129.8, 111.1, 106.8, 38.1, 21.0. Anal. Calcd. for $C_{14}H_{16}N_2Se$: C, 57.73; H, 5.54; N, 9.61. Found: C, 57.54; H, 5.36; N, 9.44.

4-Methylphenyl (*E*)-styryl selenide 3v. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51-7.48 (m, 2H), 7.35-7.12 (m, 8H), 6.84 (d, J = 16.0 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.7, 134.2, 133.2, 133.1, 130.3, 130.2, 128.7, 127.5, 126.1, 120.4, 21.2. Anal. Calcd. for $C_{15}H_{14}Se$: C, 65.93; H, 5.16. Found: C, 65.66; H, 5.29.

4-Chlorophenyl 4-methoxyphenyl selenide 3w. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.0, 136.6, 132.6, 132.2, 131.6, 129.3, 119.6, 115.3, 55.3. Anal. Calcd. for $C_{13}H_{11}OClSe$: C, 52.44; H, 3.72. Found: C, 52.19; H, 3.53.

4-Chlorophenyl 4-cyanophenyl selenide 3x. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.37-7.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.2, 136.8, 135.6, 132.5, 130.5, 130.2, 125.9, 118.6, 110.1. Anal. Calcd. for $C_{13}H_8NClSe$: C, 53.34; H, 2.75; N, 4.78. Found: C,

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53.06; H, 2.86; N, 4.55.

4-Chlorophenyl (6-dimethylamino-3-pyridyl) selenide 3y. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.37 (s, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 8.8 Hz, 1H), 3.13 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.8, 154.5, 144.6, 132.3, 131.2, 129.2, 128.9, 110.1, 106.8, 38.1. Anal. Calcd. for $C_{13}H_{13}N_2ClSe$: C, 50.09; H, 4.20; N, 8.98. Found: C, 49.83; H, 4.31; N, 8.74.

4-Chlorophenyl (*E*)-styryl selenide 3z. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53-7.47 (m, 2H), 7.37-7.29 (m, 7H), 7.16 (d, J = 15.6 Hz, 1H), 6.92 (d, J = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 136.8, 136.0, 133.8, 133.7, 129.6, 128.8, 128.5, 127.9, 126.2, 118.7. Anal. Calcd. for $C_{14}H_{11}ClSe$: C, 57.25; H, 3.77. Found: C, 57.41; H, 3.56.

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