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Copper Nanoparticles Catalyzed Se(Te)–Se(Te) Bond Activation: A Straightforward Route Towards Unsymmetrical Organochalcogenides from Boronic Acids

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A highly porous copper metal–organic framework, $[Cu_3(BTC)_2]$ (BTC = benzene-1,3,5-tricarboxylate) was synthesized and used as a precursor for the synthesis of copper nanoparticles (NPs) and characterized by several techniques, including XRD, SEM, TEM, EDX and BET measurements. The as-synthesized copper nanoparticles were immobilized onto activated charcoal (AC) by means of ultrasonication at room temperature without any pretreatment. The Cu NPs/AC was employed as a heterogeneous catalyst for the cross-coupling of diphenyl diselenide and boronic acids to form diphenyl selenides through Se–Se bond activation under ligand-, base-, and additive-free conditions. The copper NPs/AC, which combines the architecture of MOFs and the high surface area of charcoal, could be an efficient heterogeneous catalytic system that is compatible with a variety of substituents on diphenyl selenides. Its promising catalytic activity relative to that of other homogeneous systems and low catalyst loading for the synthesis of unsymmetrical diaryl selenides is an important application in the area of nanocatalysis. The Cu NPs/AC catalyst, which exhibits excellent catalytic activity and remarkable tolerance to a wide variety of substituents, led to Se sp^3-, sp^2-, and sp-carbon bond formation by using DMSO as a solvent and atmospheric air as oxidant. This approach can also be extended to the preparation of unsymmetrical organotelluride derivatives.

Copper catalysts for cross-coupling reactions are an intense field of research because they are cost-effective and hold promise for the replacement of expensive metal sources for industrial purposes. Over the past decade, the construction of carbon–selenium bonds has been an intriguing topic for researchers and the number of related publications has increased exponentially to date, mainly owing to the important therapeutic characteristics of these bonds, such as their antimicrobial, antiviral, antitumor, and antioxidant properties. In addition, chalcogens are important constituents of functional groups in biomolecules (i.e., those associated with redox chemistry) in eukaryotic biochemistry.[1] Moreover, selenium-based ionic liquids have proven to be efficient catalysts in reactions such as the carbonylation of aniline, oxidation of thiols, syntheses of octahydroacridines and thioacetals, and the Baylis–Hillman reaction of aldehydes and electron-deficient alkenes.[2–7] Over the past decade, extensive work has been devoted to developing new methodologies for the creation of bonds between sp^3-, sp^2-, sp-carbon atoms and organochalcogens, especially selenium- and tellurium-based compounds. To synthesize these moieties, a number of synthetic methods have been reported so far.[8–22] Of these, two methods are generally used. These methods involve the use of diphenyl diselenide (telluride) as starting precursor owing to its stability in air, environmental friendliness, and commercial availability. Diphenyl diselenide can be reacted with either aryl halides or boronic acids to synthesize organochalcogen derivatives. Organoboronic acids and their esters are commercially available with a variety of substituents, and they are stable and nontoxic, whereas aryl halides are difficult to activate because they require high equivalents of a base and/or reductant as additives.[23–28]

Therefore, the coupling of diphenyl diselenide and organoboronic acids is an easy route to the synthesis of unsymmetrical organochalcogenides. To achieve this, the use of inexpensive and low-toxicity copper catalysts for these transformations is more desirable in terms of atom economy, cost-effectiveness, and efficiency. To date, several research groups have produced aryl selenides by using copper salts in combination with ligands and other additives, along with long reaction times, high temperatures, and high catalyst loadings. Most of these metal-catalyzed reactions are homogeneous; therefore, the catalyst cannot be recycled. This factor may increase the cost and limit the scope of applications. It is highly desirable to develop a new catalytic system that is tolerable wide range of functional groups in the absence of base, reducing agent, and other additives.

The field of nanocatalysis[29–31] (i.e., the use of nanoparticles (NPs) to catalyze reactions) has experienced explosive growth over the past decade in both homogeneous and heterogeneous catalysis. NPs have a larger surface-to-volume ratio than bulk metals and low-coordinated sites, which enhances their activity and selectivity for a variety of transformations. In particular, metal NPs immobilized on solid supports enable easier recovery and reuse of the catalysts and have higher stability and better dispersion of the particles. Keeping this in mind, we decided to use activated charcoal,[32,33] which is commercially available and cost-effective for industrial purposes, as a solid support.

As a continuation of our ongoing efforts to discover new nanoparticles[34–37] as heterogeneous catalysts in organic synthesis, we report herein that the copper NPs prepared from

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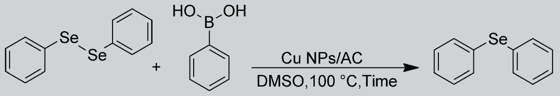
$[Cu_3(BTC)_2]$ show excellent catalytic activity for the cross-coupling of diphenyl dichalcogenide and a variety of organoboronic acids, in terms of yield, short reaction time, and additive-free conditions, by using DMSO as a solvent under an air atmosphere. Metal–organic frameworks (MOFs) have attracted much attention over the past decade because of their uniform crystalline structure, high porosity, large surface area, and high thermal and chemical stability. The application of MOFs in gas storage, CO_2 separation, sensors, and other areas has been well explored. Of course, there is a particular interest in the use of MOFs as catalysts. So far, various types of MOFs with different architectures have been reported for catalytic organic reactions.[38–43] Our current interest lies in a basic copper MOF, $[Cu_3(BTC)_2]$, and its application as a catalyst in the preparation of organochalcogens.[44,45] However, there are some drawbacks with $[Cu_3(BTC)_2]$ that must be accounted for; for example, the direct use of $[Cu_3(BTC)_2]$ as a catalyst in organic transformations could require purification of the desired product because of contamination and solubility issues with the reaction under thermal conditions.

Therefore, in this report, we demonstrate that the copper NPs derived from $[Cu_3(BTC)_2]$ show an excellent catalytic activity for the synthesis of organochalcogen derivatives. The as-synthesized copper NPs immobilized on activated carbon (AC), which is a simple, inexpensive and high surface area support that can serve as an efficient heterogeneous catalyst for the same transformation. In 2005, Wang et al.[46] first reported a simple CuI-catalyzed synthesis of diaryl selenides and tellurides from arylboronic acids. Subsequently, Taniguchi[47] used CuI with the combination of a bipyridyl ligand to prepare a variety of unsymmetrical organochalcogenides. Braga and co-workers[48] described the use of commercially available CuO nanopowder as a catalyst to prepare diaryl selenides. In 2009, Ren et al.[49] explored Lewis acid $InBr_3$-mediated direct cross-coupling of arylboronic acids with diorganodiselenides and ditellurides. Ranu[50] and co-workers reported the coupling of organoboronic acids and dichalcogenides catalyzed by $CuFe_2O_4$. The Alves group[51] found that glycerol acted as a green solvent to promote the CuI-catalyzed cross-coupling of diaryl diselenides with aryl boronic acids by using DMSO as an additive. Xu and co-workers[52] demonstrated the copper-salt-catalyzed preparation of diphenyl selenides in the presence of base and ligand. Recently, Kumar[53] used copper-salt-catalyzed preparation of diphenyl chalcogenides in the presence of base, ligands, and reducing agents. Bhadra et al.[54] introduced alumina-supported copper-mediated nucleophilic displacement of phenylselenium bromide as an alternative precursor for the synthesis of different kinds of aryl selenides. Lenardo and co-workers[55] disclosed the use of imidazolium ionic liquids for the synthesis of diaryl selenides from electrophilic selenium species and nucleophilic boron reagents under a N_2 atmosphere. Recently, transition-metal-free unsymmetrical diaryl chalcogenides from arenes and dichalcogenides has been reported by using persulfate oxidant and trifluoroacetic acid solvent.[56]

The cross-coupling reaction between diphenyl diselenide and phenyl boronic acid in DMSO solvent by using copper NPs on charcoal as a catalyst generated diphenyl selenide as the desired product.

Initially, diphenyl diselenide and phenyl boronic acid were selected as substrates to determine the optimal reaction conditions. The results are summarized in Table 1. The control experiments showed that only a 5% yield was obtained when the reaction was performed in the absence of the catalyst (Table 1, entry 1), and no coupled product was detected when the reaction was performed at room temperature for 12 h with 4 mol% of the catalyst (Table 1, entry 2). Then, we screened experimental conditions at a constant catalyst concentration of 4 mol%. Increasing the temperature from room temperature to 80 °C for 3 h afforded a 32% yield (Table 1, entry 3), whereas a lower catalyst loading reduced the product yield (Table 1, entry 4). The highest yield (i.e., complete disappearance of diphenyl diselenide without any side products according to GC-MS analysis) was achieved with 4 mol% of copper nanoparti-

Table 1. Optimization of the cross-coupling of diphenyl diselenide with phenylboronic acid catalyzed by copper nanoparticles on charcoal.[a]



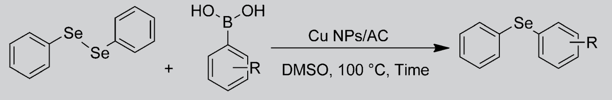
Entry	Solvent[b]	Catalyst [mol% Cu]	Temp [°C]	Yield[c] [%]
1	DMSO	–	100	5
2	DMSO	4	RT	ND
3	DMSO	4	80	32
4	DMSO	3	100	93
5	DMSO	4	100	100
6	DMSO	4	100	traces[d]
7	DMF	4	100	97
8	DMA	4	100	91
9	NMP	4	100	89
10	DMPU	4	100	95
11	dioxane	4	reflux	15
12	[BMIM][BF_4]	4	100	8
13	glycerol	4	100	3
14	PEG	4	100	13
15	EG	4	100	7
16	DMC	4	reflux	ND
17	toluene	4	100	ND
18	DMSO	CuO hollow spheres[e]	100	84
19	DMSO	Cu_2O cubes[f]	100	89
20	DMSO	Cu nanoparticles[g]	100	74
21	DMSO	recovered from entry 5	100	100
22	DMSO	recovered from entry 21	100	100
23	DMSO	recovered from entry 22	100	89
24	DMSO	recovered from entry 23	100	80
25	DMSO	recovered from entry 24	100	73

[a] Optimized Reaction Conditions: diphenyl diselenide (0.64 mmol), phenylboronic acid (1.41 mmol), 4 mol% of Cu NPs/C with respect to diphenyl diselenide, $T = 100\,^{\circ}C$, $t = 3$ h; [b] 1 mL solvent was used; [c] conversion yields were determined from GC-MS analysis; [d] reaction under N_2 atmosphere; [e–g] copper catalysts prepared according to previous reports.

cles catalyst in DMSO solvent at 100 °C within a short time (Table 1, entry 5). The same experiment in DMSO solvent with bubbling nitrogen afforded only traces of the product (Table 1, entry 6); therefore, air was indispensable to the reaction. Other solvent systems, including *N,N′*-dimethylformamide (DMF), *N,N′*-dimethylacetamide (DMA), *N*-methyl pyrrolidinone (NMP), and *N,N′*-dimethylpropylene urea (DMPU), also provided satisfactory results (Table 1, entries 7–10). Solvents such as dioxane, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) ionic liquid, glycerol, polyethylene glycol (PEG), ethylene glycol (EG), dimethyl carbonate (DMC), and toluene led to diminished yield of the product (Table 1, entries 11–17). To identify the advantages of our copper nanoparticles/charcoal catalyst, we studied the effect of other homogeneous copper sources (4 mol % copper content), such as CuO hollow spheres,[20] Cu_2O cubes,[21a,b] and copper NPs.[22] These reactions also proceeded well, but did not deliver the product in as high yield as the copper NPs synthesized from [$Cu_3(BTC)_2$] (Table 1, entries 18–20) under the same experimental conditions. A reusability study of the cross-coupling of diphenyl diselenide and phenyl boronic acid was performed separately by using the optimized conditions; the results are summarized in Table 1 (entries 21–25).

Next, to further examine the substrate scope, diphenyl diselenide, dibenzyl diselenide, and diphenyl ditelluride with various substituted boronic acids were examined under optimal conditions (Table 2, Table 3, and Table 4). The cross-coupling of diphenyl diselenide was first examined with various substituted arylboronic acids (Table 2, entries 1–15). Products with the electron-donating groups methoxy, methyl, and 2,4,6-trimethyl phenylboronic acids were generated in 100, 100, and 97 % yields, respectively (Table 2, entries 1–3), whereas 2,6-dimethoxy phenylboronic acid was furnished in a moderate yield (Table 2, entry 4). Strong electron-withdrawing groups, such as naphthyl, and groups on the phenylboronic acids, including 4-acetyl, 4-ethoxycarbonyl, 4-trifluoromethyl, 4-cyano, 4-biphenyl, and even 2-formyl, were well-tolerated by our catalytic system. In the case of halogen-containing phenylboronic acids, coupling occurred smoothly to afford the corresponding arylated phenylselenide products (Table 1, entries 12 and 13). Heterocyclic boronic acids were also generated from their cor-

Table 2. The coupling reactions of diphenyl diselenide with various boronic acids catalyzed by Cu NPs/C.[a]



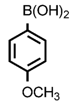
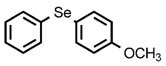
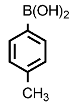
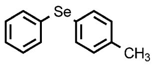
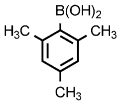
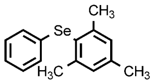
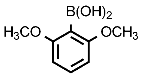
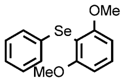
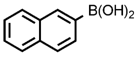
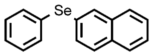
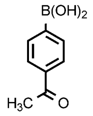
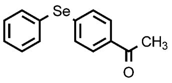
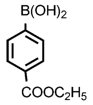
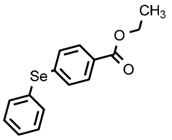
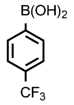
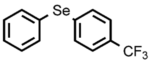
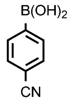
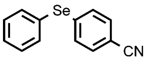
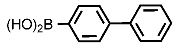
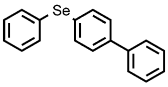
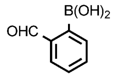
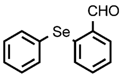
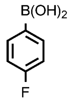
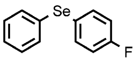
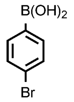
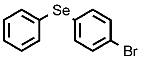
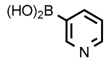
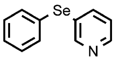
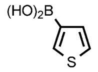
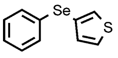
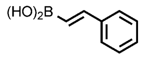
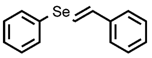
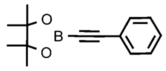
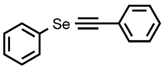
Entry	Boronic acid	Product	Time [h]	Yield [%][b]
1			3	100
2			4	100
3			6	97
4			6	61
5			5	100

Table 2. (Continued)

Entry	Boronic acid	Product	Time [h]	Yield [%][b]
6			6	94
7			6	99
8			6	100
9			6	96
10			6	99
11			9	100
12			6	95
13			4	100
14			6	99
15			6	100
16			6	100 (99:1)[d]
17			6	99

[a] Reaction conditions: diphenyl diselenide (0.64 mmol), substituted phenylboronic acid (2.2 equiv.), catalyst (4 mol % Cu), DMSO (1 mL), 100 °C; [b] yield was determined from average of two independent runs by GC-MS. [c] *trans*-2-phenylvinylboronic acid, Aldrich catalogue No. 473790; [d] selectivity (*E*:*Z*, 99:1) by GC-MS. [e] 2-phenyl-1-ethynylboronic acid pinacol ester, Aldrich catalogue No. 686808.

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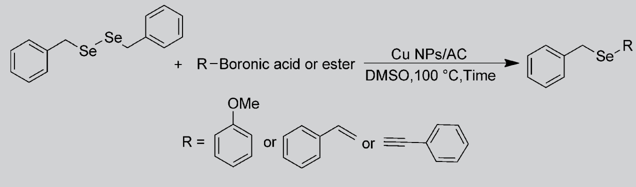
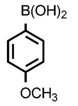
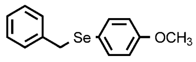
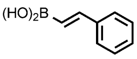
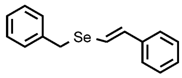
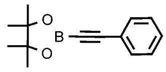
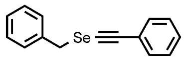
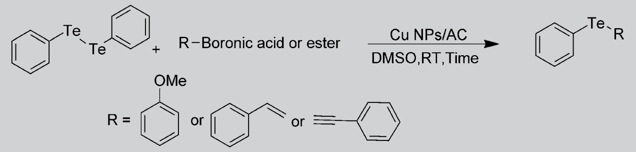
Table 3. Catalyst efficiency studies with dibenzyl diselenide and substituted boronic acids and esters catalyzed by Cu NPs/C.[a]

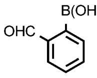
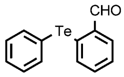
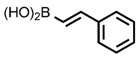
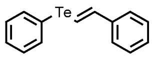
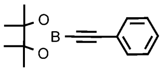
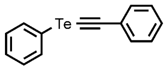


Entry	Boronic acid	Product	Time [h]	Yield [%]
1			5	94
2			5	100 (100)[b]
3			6	100

[a] Reaction conditions: same as in Table 2; [b] selectivity (100% *E* isomer) by GC-MS.

Table 4. Extension of catalytic application to reactions of diphenyl ditelluride[a]



Entry	Boronic acid	Product	Time [h]	Yield [%]
1			18	100
2			18	100 (100)[b]
3			18	30, 100[c]

[a] Reaction conditions: diphenyl ditelluride (0.48 mmol), substituted boronic acid or ester (2.2 equiv.), catalyst (4 mol% Cu) with respect to diphenyl ditelluride, DMSO (1 mL), RT, 18 h; [b] Selectivity (100% *E* isomer); [c] Reaction at 100 °C, 6 h.

responding cross-coupled product in excellent yields (Table 2, entries 14 and 15). Remarkably, our catalytic system was also highly compatible with *trans*-2-phenylvinylboronic acid and the 2-phenyl-1-ethynylboronic acid pinacol ester afforded (*E*) and (*Z*)-(styryl)(phenyl)selenide (*E/Z*, 99:1) and phenyl(phenylethynyl)selane in 99 and 100% yields, respectively (Table 2, entries 16 and 17).

The applicability of this methodology was also extended to dibenzyl diselenide instead of diphenyl diselenide for the reaction with 4-methoxyphenylboronic acid. Surprisingly, the reaction supplied the cross-coupled product in an excellent yield (Table 3, entry 1). Similarly, reactions with *trans*-2-phenylvinylboronic acid and 2-phenyl-1-ethynylboronic acid pinacol ester also gave good yields in a short time under the same experimental conditions as shown in Table 2 (Table 3, entries 2 and 3).

Prompted by these outstanding results, we discovered that our catalyst was applicable to the synthesis of a variety of telluride derivatives at room temperature (Table 4). Firstly, the catalytic activity was tested in a reaction of diphenyl ditelluride with sterically hindered and electron-withdrawing 2-formylphenylboronic acid at room temperature for 18 h, which afforded phenyl(2-formylphenyl)tellane with complete conversion and no side products (Table 4, entry 1). An alternative coupling partner, *trans*-2-phenylvinylboronic acid, also provided the coupled product in excellent yield at room temperature with complete *trans* selectivity (Table 4, entry 2). The yield was reduced to 30% when 2-phenyl-1-ethynylboronic acid pinacol ester was reacted at room temperature; however, the yield increased considerably to 100% when the reaction was performed at 100 °C for 6 h (Table 4, entry 3). To the best of our knowledge, this is the first report of the synthesis of organotellurium derivatives from boronic acids at room temperature without any additives.

[$Cu_3(BTC)_2$] was synthesized by a solvothermal method according to a literature procedure. The as-synthesized [$Cu_3(BTC)_2$] was used as a precursor for the preparation of copper NPs by using a chemical-reduction technique. The obtained Cu NPs were characterized by energy-dispersive spectrometry (EDS), TEM, XRD, and X-ray photoelectron spectroscopy (XPS). Nitrogen adsorption–desorption isotherm measurements were performed on a Tristar II 3020 V1.03 at −196 °C. The BET equation was used to determine the specific surface area, pore volume, and pore size of the Cu NPs/AC.

The EDS measurement shown in Figure 1 (with inset SEM image) indicated the presence of a small amount of oxygen as well as elemental copper in the prepared copper NPs, this finding might indicate an oxidized layer of copper on the surfaces of the particles. The TEM images show that the surfaces of the Cu NPs were coated with Cu_2O, which is probably because of oxidation of copper NPs in air. The particles were regular polyhedral shape and almost monodisperse, some particles appeared as a Cu core and a Cu_2O shell formed from oxidized Cu NPs (Figure 2a). TEM topography revealed that the particles

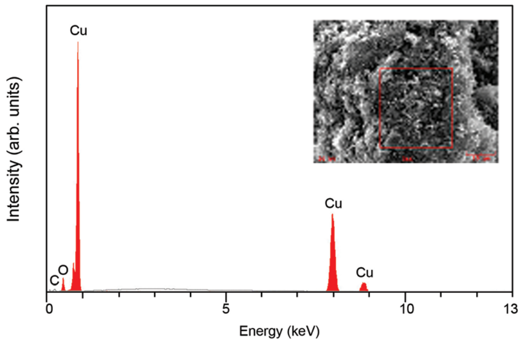


Figure 1. EDS analysis of Cu NPs with an inset SEM image (scale bar = 10 μm).

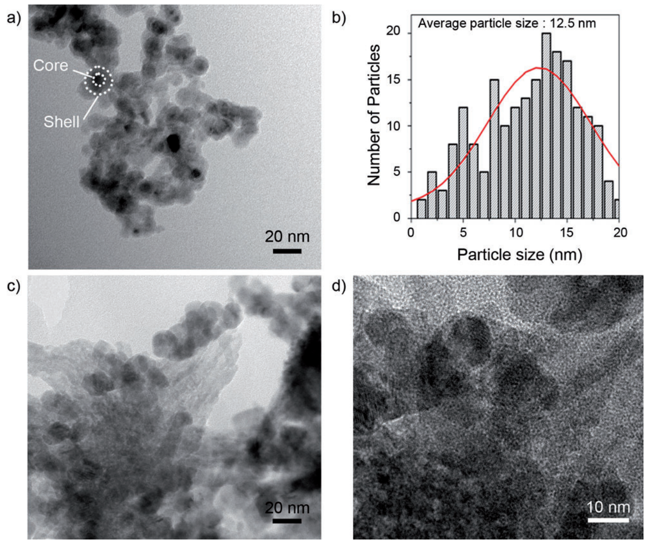


Figure 2. a) Cu_2O-coated Cu NPs, b) size-distribution graph of nanoparticles, c) copper nanoparticles immobilized on charcoal d) HRTEM image of Cu NPs/C.

were approximately 12.5 nm (Figure 2b) and immobilized on activated charcoal (Figure 2c). The high-magnification TEM image of Cu NPs/AC (Figure 2d) revealed that the NPs were well-dispersed on the charcoal. The powder XRD pattern of these precipitates showed the presence of metallic copper. The average grain size (D) of the NPs was calculated from the X-ray diffraction data by using Scherrer's formula: $D=0.9k/(B\cos\theta B)$, in which k is the X-ray wavelength used for the diffraction experiments (Cu-$K_\alpha = 1.5406$ Å), B is the full-width at half-maximum of a particular peak (in radians), and θB is the peak position. For the (111) peak, we found the grain size normal to the scattering plane to be approximately 9.6 nm. The X-ray diffraction pattern shown in Figure 3 reveals that a Cu_2O shell was formed by oxidation of the copper core in air. The three main peaks at $\theta = 43.2$, 50.3, and 74.1° were assigned to the reflections of the (111), (002), and (022) planes in the Cu phase (JCPDS No. 04-0836, Figure 3a) together with small peaks, corresponding to (111) and (220) planes in the Cu_2O phase. Bulk copper (Figure 3b) and Cu_2O (JCPDS No. 77-0199, Figure 3c) are shown for comparison.

The XPS spectrum of Cu NPs is depicted in Figure 4. As expected, Cu NPs display two main peaks at 932.8 and 953.7 eV, which are due to the binding energy of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The difference between binding energies of Cu and Cu_2O is very small and differs only by 0.1–0.2 eV. Therefore, the accurate determination and differentiation of Cu and Cu_2O seems to be impossible by XPS analysis.

The BET surface area of Cu NPs/AC was found to be 654.0 $m^2\,g^{-1}$ and the desorption branch of isotherm was used for the Barrett-Joyner-Halenda (BJH) calculation to measure pore volume and pore size. The values are 0.268 $cm^3\,g^{-1}$ and 3.9 nm. The N_2-sorption isotherm of the Cu NPs/AC is depicted in Figure 5. It can be seen that copper nanoparticles on charcoal exhibit a Langmuir type IV isotherm, which corresponds to high-surface-area mesoporous materials. The high catalytic activity of copper nanoparticles on charcoal can be ascribed to the high surface area, enriched dispersion, and sufficient adsorption of reactants, which leads to the enhancement of catalytic performance.

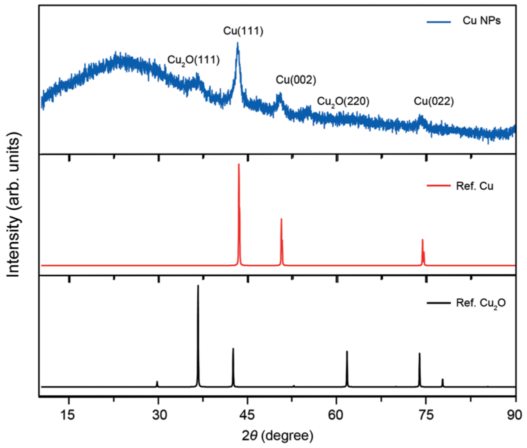


Figure 3. XRD pattern of a) Cu NPs synthesized from $[Cu_3(BTC)_2]$, b,c) corresponds to bulk copper and Cu_2O for reference.

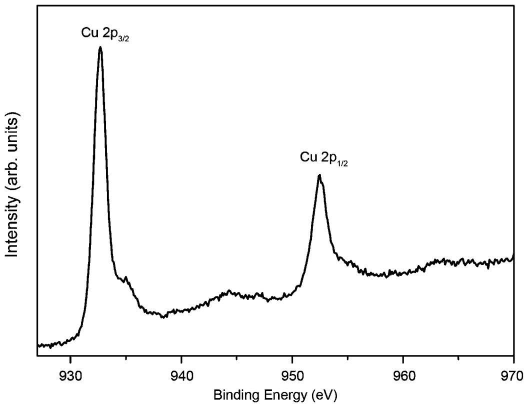


Figure 4. XPS spectrum of the copper nanoparticles.

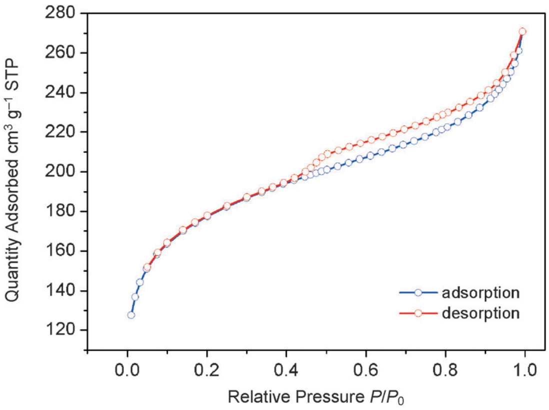


Figure 5. N_2-adsorption–desorption isotherm of copper nanoparticles/AC.

The heterogeneity of Cu NPs/AC was examined by using a hot-filtration test and ICP analysis. The reaction between di-

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phenyl diselenide and 2-formylphenylboronic acid was chosen for the hot-filtration test. Copper leaching into the hot filtrate was determined to be approximately 0.0005 % by inductively coupled plasma–optical emission spectrometry (ICP-OES) analysis. The reaction was stopped at 43 % conversion and filtered. The reaction mixture was divided into two portions. Continuation of the reaction in two portions under the same conditions at 100 °C for a further 6 h resulted in 99 % (GC-MS) conversion of the portion containing Cu NPs/AC; in the absence of catalyst the conversion reached only 49 % (from the original 43 %). Thus, the catalytic reaction should be considered to be predominantly heterogeneous.

To confirm the necessity and role of copper in promoting the cross-coupling, we reacted dibenzyl diselenide with excess CuNPs/AC (1.2 equiv.) in the absence of phenylboronic acid under the same experimental conditions. During the reaction, a solid intermediate, [$(PhCH_2Se)_2$-Cu)], precipitated and was isolated by centrifugation using ethanol several times. The GC-MS analysis of the combined supernatant solution (after centrifugation) revealed the complete absence of dibenzyl diselenide starting material. XPS analysis of the intermediate, as shown in Figure 6, suggested the presence of a bond between copper (932.7, 952.7 eV) and selenium (53.6 eV). The intermediate was insoluble in all solvents, which inhibited the additional characterization and separation of the solid intermediate from unreacted CuNPs/AC. The EDS analysis further confirmed that the intermediate contained a Cu–Se bond (Figure 7). Surprisingly, further reaction of the solid intermediate with phenylboronic acid in DMSO solvent provided only 30 % of the cross-coupled product (benzyl phenyl selenide, Scheme 1). The same observation for sulfides was noticed and reported by Taniguchi in 2007; he proposed that the yield was reduced because of insufficient oxidant or poor solubility and could be improved, to some extent, through the use of additives.[47]

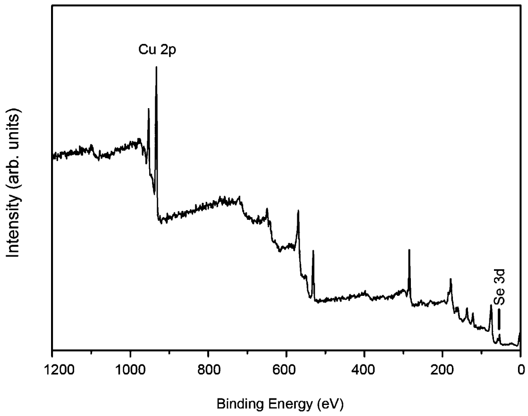


Figure 6. XPS spectrum of the intermediate.

The recyclability of the catalyst was assessed for the coupling reaction between diphenyl diselenide and phenylboronic acid to produce diphenylselenide at 100 °C with 4 mol % of Cu (Figure 8). The first two runs of the reaction provided complete conversion (Table 1, entries 21 and 22), but the catalytic activity dropped slightly in the subsequent runs (Table 1, entries 23–25). The decreased catalytic activity was because of oxidation of copper NPs in air, which was indispensable in the reaction because it acted as an oxidant. It should be noted that the reaction flushed with nitrogen rendered only traces of the coupled product (Table 1, entry 6). In addition, a TEM image of Cu NPs/AC after three uses is shown in Figure 9. The image shows severe aggregation of the Cu nanoparticles at high reaction temperature, suggesting that the decreased catalytic activity may largely be due to the agglomeration of copper nanoparticles into larger colloids.

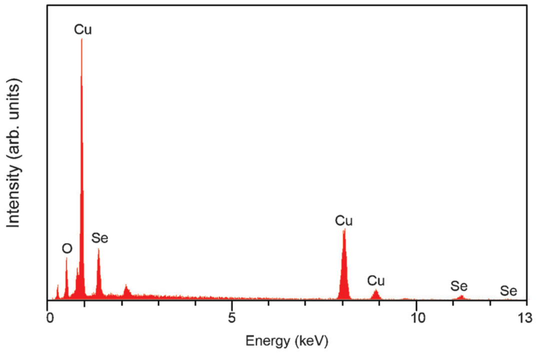
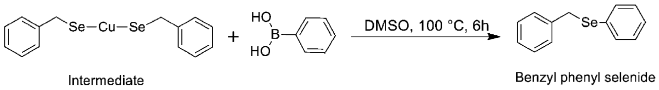


Figure 7. EDS spectrum of the intermediate.



Scheme 1. Coupling of intermediate with phenylboronic acid.

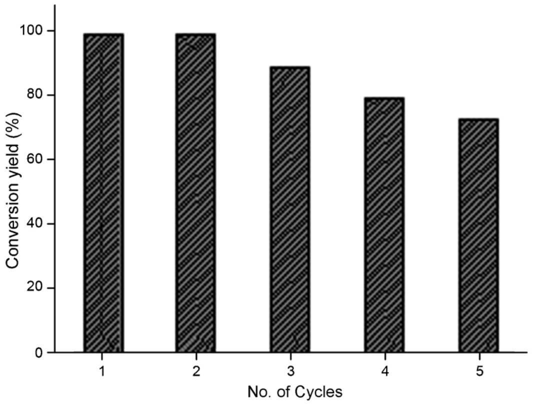


Figure 8. Recycle performance of copper nanoparticles in the cross-coupling reaction of diphenyl diselenide with phenylboronic acid.

In conclusion, highly catalytically active copper NPs were synthesized without the use of surfactants and stabilizers by the reaction of [$Cu_3(BTC)_2$] and $NaBH_4$ by a simple chemical-reduction method and characterized by XRD, TEM, SEM, and XPS analyses. These inexpensive nanoparticles were used as an efficient heterogeneous catalyst for the cross-coupling reaction of diphenyl dichalcogenides with boronic acids to generate multipurpose metal–carbon bonds in the absence of additives. The

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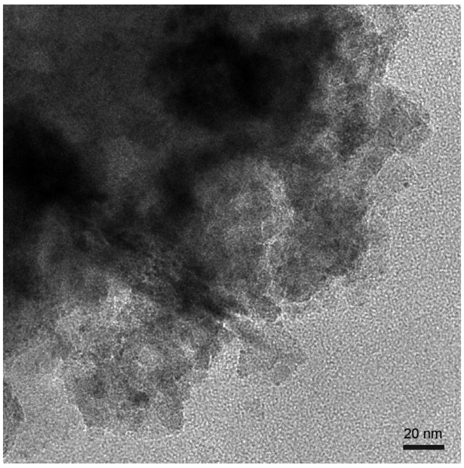

Figure 9. TEM analysis of copper nanoparticles/AC after three cycles.

nanoparticles were three-in-one catalysts owing to the formation of Se(Te)-sp^3, Se(Te)-sp^2, and Se(Te)-sp bonds. The copper nanoparticles from Cu-MOF offered higher catalytic activity than CuO hollow spheres, Cu_2O nanocubes, and Cu NPs. It should be noted that the cross-coupling reaction of diphenyl dichalcogenide and boronic acids could only proceed in the presence of the solid copper nanoparticles catalyst, and there was no participation from leached copper species present in the reaction solution. The protocol offers significant advantages, such as simple synthesis of the catalyst, mild reaction conditions, compatibility for various substrates, and reusability of the catalysts.

Experimental Section

Materials and instrumentation

All commercial reagents and starting materials were purchased from Sigma–Aldrich and TCI and used without further purification. The products reported are known and their mass spectra were confirmed by using Shimadzu GCMS-QP 2010 Ultra (Pusan National University). TEM samples (FEI, Tecnai F30 Super-Twin, National Nanofab Center, South Korea) were prepared by placing a few drops of the corresponding colloidal solution on carbon-coated copper grids (200 mesh, F/C coated, Ted Pella Inc., Redding, CA, USA). SEM was performed by using a SEM (VEGA3, TESCAN). The elemental analysis was performed by using EDS (550i, IXRF Systems, Inc.). The XRD patterns were recorded by a Rigaku GDX-11P3A diffractometer (Pusan National University). N_2-adsorption isotherm was measured at −196 °C on a Tristar II 3020 V1.03 machine. ICP-OES analysis was determined by using Thermoscientific icap 6300 ICP spectrometer.

General procedure for cross-coupling reactions

Diphenyl diselenide (0.32 mmol, 100 mg), phenylboronic acid (0.71 mmol, 86 mg), Cu NPs (4 mol% with respect to diphenyl diselenide), and DMSO (1 mL) were added to a 10 mL aluminium-capped vial. The mixture was sonicated for 5 min at RT and then placed in a preheated oil bath at 100 °C with magnetic stirring. The reaction was monitored by TLC. After being cooled to RT, diluted with diethyl ether, and filtered through a Celite bed, the filtrate was washed with water and KOH solution (to remove excess phenylboronic acid). The solution was extracted with ether (and washed with brine wash when necessary); the combined ether layer was then dried over anhydrous magnesium sulfate, filtered, evaporated by using a rotary evaporator, and dried under high vacuum. The crude product was subjected to GC-MS analysis.

Synthesis of [$Cu_3(BTC)_2$]

[$Cu_3(BTC)_2$] was synthesized by using a solvothermal method from slightly modified literature procedure.[61] Typically, a mixture of $Cu(NO_3)_2 \cdot 2.5\,H_2O$ (10 g, 43 mmol) and H_3BTC (5 g, 23 mmol) was dissolved in a mixture of solvents DMF/EtOH/H_2O (250 mL, 1:1:1) and stirred for 10 min. The mixture was heated at 85 °C for 20 h and, after cooling to RT, underwent centrifugation for 20 min at 10 000 rpm. Then, the solid product was removed by decanting the mother liquor and washed with DMF, followed by dichloromethane three times in three days. The product was then dried under high vacuum to yield blue crystals.

Synthesis of copper nanoparticles/AC

Freshly prepared $NaBH_4$ (0.312 g, 82.66 mmol) in water (5 mL) was added dropwise to [$Cu_3(BTC)_2$] (0.5 g, 0.8266 mmol) in water (20 mL) under cooling and stirring for 10 min. Stirring was continued for another 30 min, followed by centrifugation at 10 000 rpm for 20 min. After decanting the mother liquor, the obtained solid black precipitate was copiously washed with deionized water and then ethanol, dried under high vacuum to afford black powder. The black powder was added to the mixture of ethanol and activated charcoal, followed by ultrasonication at RT for 30 min and then heated at reflux temperature for 6 h under vigorous magnetic stirring. Next, the particles/AC was centrifuged three times with ethanol at 10 000 rpm for 20 min. The immobilized particles on activated charcoal were dried under vacuum. The copper loading on activated charcoal was approximately 33.1 % measured by ICP-OES analysis.

Acknowledgements

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Keywords: copper · cross-coupling · diphenyl dichalcogenide · heterogeneous catalysis · nanoparticles

[1] C. Jacob, G. I. Giles, N. M. Giles, H. Sies, *Angew. Chem. Int. Ed.* **2003**, *42*, 4742–4758; *Angew. Chem.* **2003**, *115*, 4890–4907.
[2] H. S. Kim, Y. J. Kim, H. Lee, K. Y. Park, C. Lee, C. S. Chin, *Angew. Chem. Int. Ed.* **2002**, *41*, 4300–4303; *Angew. Chem.* **2002**, *114*, 4476–4479.
[3] S. Thurow, V. A. Pereira, D. M. Martinez, D. Alves, G. Perin, R. G. Jacob, E. J. Lenardo, *Tetrahedron Lett.* **2011**, *52*, 640–643.
[4] E. J. Lenardão, S. R. Mendes, P. C. Ferreira, G. Perin, C. C. Silveira, R. G. Jacob, *Tetrahedron Lett.* **2006**, *47*, 7439–7442.

[5] E. J. Lenardão, E. L. Borges, S. R. Mendes, G. Perin, R. G. Jacob, *Tetrahedron Lett.* **2008**, *49*, 1919 – 1921.
[6] E. J. Lenardão, J. O. Feijo, S. Thurow, G. Perin, R. G. Jacob, C. C. Silveira, *Tetrahedron Lett.* **2009**, *50*, 5215 – 5217.
[7] D. M. Freudendahl, S. Santoro, S. A. Shahzad, C. Santi, T. Wirth, *Angew. Chem. Int. Ed.* **2009**, *48*, 8409 – 8411; *Angew. Chem.* **2009**, *121*, 8559 – 8562.
[8] Y. Nishiyama, K. Tokunaga, N. Sonoda, *Org. Lett.* **1999**, *1*, 1725 – 1727.
[9] S. Pariagh, K. M. Tasker, F. H. Fry, A. L. Holme, C. A. Collins, N. Okarter, N. Gutowski, C. Jacob, *Org. Biomol. Chem.* **2005**, *3*, 975 – 980.
[10] G. Perin, E. J. Lenardao, R. G. Jacob, R. B. Panatieri, *Chem. Rev.* **2009**, *109*, 1277 – 1301.
[11] G. Zeni, D. S. Ludtke, R. B. Panatieri, A. L. Braga, *Chem. Rev.* **2006**, *106*, 1032 – 1076.
[12] R. J. Cohen, D. L. Fox, R. N. Salvatore, *J. Org. Chem.* **2004**, *69*, 4265 – 4268.
[13] D. M. Freudendahl, S. A. Shahzad, T. Wirth, *Eur. J. Org. Chem.* **2009**, 1649 – 1664.
[14] B. C. Ranu, K. Chattopadhyay, S. Banerjee, *J. Org. Chem.* **2006**, *71*, 423 – 425.
[15] H. J. Cristau, B. Chabaud, R. Labaudiniere, H. Christol, *J. Org. Chem.* **1986**, *51*, 875 – 878.
[16] Y. Nishiyama, H. Kawamatsu, S. Funato, K. Tokunaga, N. Sonoda, *J. Org. Chem.* **2003**, *68*, 3599 – 3602.
[17] C. C. Silveira, P. C. S. Santos, S. R. Mendes, A. L. Braga, *J. Organomet. Chem.* **2008**, *693*, 3787 – 3790.
[18] X. Huang, L. S. Zhu, *J. Organomet. Chem.* **1996**, *523*, 9 – 11.
[19] H. Zhao, W. Hao, Z. Xi, M. Cai, *New J. Chem.* **2011**, *35*, 2661 – 2665.
[20] M. Bonaterra, S. E. Martin, R. A. Rossi, *Tetrahedron Lett.* **2006**, *47*, 3511 – 3515.
[21] J. H. Cheng, C. L. Yi, T. J. Liu, C. F. Lee, *Chem. Commun.* **2012**, *48*, 8440 – 8442.
[22] J. M. Becht, C. L. Drian, *J. Org. Chem.* **2011**, *76*, 6327 – 6330.
[23] K. Swapna, S. N. Murthy, Y. V. D. Nageswar, *Eur. J. Org. Chem.* **2011**, 1940 – 1946.
[24] D. Singh, E. E. Alberto, O. E. D. Rodrigues, A. L. Braga, *Green Chem.* **2009**, *11*, 1521 – 1524.
[25] Y. Li, H. Wang, X. Li, T. Chen, D. Zhao, *Tetrahedron* **2010**, *66*, 8583 – 8586.
[26] V. P. Reddy, A. V. Kumar, K. Swapna, K. R. Rao, *Org. Lett.* **2009**, *11*, 951 – 953.
[27] A. Saha, D. Saha, B. C. Ranu, *Org. Biomol. Chem.* **2009**, *7*, 1652 – 1657.
[28] A. Kumar, B. S. Bhakuni, C. D. Prasad, S. Kumar, S. Kumar, *Tetrahedron* **2013**, *69*, 5383 – 5392.
[29] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181 – 5203.
[30] B. R. Cuenya, *Acc. Chem. Res.* **2013**, *46*, 1682 – 1691.
[31] M. B. Gawande, P. S. Branco, R. S. Varma, *Chem. Soc. Rev.* **2013**, *42*, 3371 – 3393.
[32] H. Sharghi, R. Khalifeh, M. M. Doroodmand, *Adv. Synth. Catal.* **2009**, *351*, 207 – 218.
[33] F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *Org. Biomol. Chem.* **2011**, *9*, 6385 – 6395.
[34] H. R. Choi, H. Woo, S. Jang, J. Y. Cheon, C. Kim, J. Park, K. H. Park, S. H. Joo, *ChemCatChem* **2012**, *4*, 1587 – 1594.
[35] A. Kim, D. Shin, M. Kim, C. Yoon, H. Song, K. H. Park, *Eur. J. Inorg. Chem.* **2014**, 1279 – 1283.
[36] H. Woo, K. Lee, K. H. Park, *ChemCatChem* **2014**, *6*, 1635 – 1640.
[37] H. Woo, K. H. Park, *Catal. Commun.* **2014**, *46*, 133 – 137.
[38] N. T. S. Phan, T. T. Nguyen, P. H. L. Vu, *ChemCatChem* **2013**, *5*, 3068 – 3077.
[39] H. Noei, S. Amirjalayer, M. Muller, X. Zhang, R. Schmid, M. Muhler, R. A. Fischer, Y. Wang, *ChemCatChem* **2012**, *4*, 755 – 759.
[40] N. T. S. Phan, T. T. Nguyen, V. T. Nguyen, K. D. Nguyen, *ChemCatChem* **2013**, *5*, 2374 – 2381.
[41] E. Pérez-Mayoral, J. Cejka, *ChemCatChem* **2011**, *3*, 157 – 159.
[42] Y. Huang, T. Ma, P. Huang, D. Wu, Z. Lin, R. Cao, *ChemCatChem* **2013**, *5*, 1877 – 1883.
[43] T. Maity, D. Saha, S. Koner, *ChemCatChem* **2014**, *6*, 2373 – 2383.
[44] B. Mohan, S. Hwang, H. Woo, K. H. Park, *Tetrahedron* **2014**, *70*, 2699 – 2702.
[45] B. Mohan, S. Hwang, S. Jang, K. H. Park, *Synlett* **2014**, *25*, 2078 – 2082.
[46] L. Wang, M. Wang, F. Huang, *Synlett* **2005**, *13*, 2007 – 2010.
[47] N. Taniguchi, *J. Org. Chem.* **2007**, *72*, 1241 – 1245..
[48] D. Alves, C. G. Santos, M. W. Paixao, L. C. Soares, D. Souza, O. E. D. Rodrigues, A. L. Braga, *Tetrahedron Lett.* **2009**, *50*, 6635 – 6638.
[49] K. Ren, M. Wang, L. Wang, *Org. Biomol. Chem.* **2009**, *7*, 4858 – 4861.
[50] D. Kundu, N. Mukherjee, B. C. Ranu, *RSC Adv.* **2013**, *3*, 117 – 125.
[51] V. G. Ricordi, C. S. Freitas, G. Perin, E. J. Lenardao, R. G. Jacob, L. Savegnago, D. Alves, *Green Chem.* **2012**, *14*, 1030 – 1034.
[52] B. Zheng, Y. Gong, H. J. Xu, *Tetrahedron* **2013**, *69*, 5342 – 5347.
[53] A. Kumar, S. Kumar, *Tetrahedron* **2014**, *70*, 1763 – 1772.
[54] S. Bhadra, A. Saha, B. C. Ranu, *J. Org. Chem.* **2010**, *75*, 4864 – 4867.
[55] C. S. Freitas, A. M. Barcellos, V. G. Ricordi, J. M. Pena, G. Perin, R. G. Jacob, E. J. Lenardao, D. Alves, *Green Chem.* **2011**, *13*, 2931 – 2938.
[56] C. D. Prasad, S. J. Balkrishna, A. Kumar, B. S. Bhakuni, K. Shrimali, S. Biswas, S. Kumar, *J. Org. Chem.* **2013**, *78*, 1434 – 1443.
[57] J. Y. Kim, J. C. Park, H. Kang, H. Song, K. H. Park, *Chem. Commun.* **2010**, *46*, 439 – 441.
[58] J. C. Park, J. Kim, H. Kwon, H. Song, *Adv. Mater.* **2009**, *21*, 803 – 807.
[59] J. Y. Kim, J. C. Park, A. Kim, A. Y. Kim, H. J. Lee, H. Song, K. H. Park, *Eur. J. Inorg. Chem.* **2009**, 4219 – 4223.
[60] B. Mohan, H. Woo, S. Jang, S. Lee, S. Park, K. H. Park, *Solid State Sci.* **2013**, *22*, 16 – 20.
[61] A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998 – 17999.

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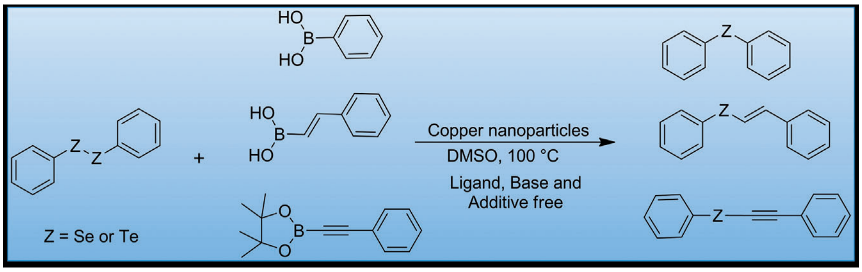

Three-in-one catalyst: Copper nanoparticles on activated charcoal show excellent catalytic activity towards the synthesis of unsymmetrical chalcogenides, starting from boronic acids, in air under ligand-, base-, and additive-free conditions, and resulting in selenium sp^3-, sp^2-, and sp-carbon bond formation.

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Copper Nanoparticles Catalyzed Se(Te)–Se(Te) Bond Activation: A Straightforward Route Towards Unsymmetrical Organochalcogenides from Boronic Acids

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