Solvent selective phenyl selenylation and phenyl tellurylation of aryl boronic acids catalyzed by Cu(II) grafted functionalized polystyrene

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Solvent selective phenyl selenylation and phenyl tellurylation of aryl boronic acids catalyzed by Cu(II) grafted functionalized polystyrene

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Abstract

A solvent-selective methodology for the phenyl selenylation and phenyl tellurylation of aryl boronic acids has been developed for the first time using a polymer supported Cu(II) catalyst. The catalyst was synthesized by anchoring Cu(OAc)$_2$ onto a functionalized polystyrene with pyridine thiosemicarbazone ligand. It was then characterized properly by SEM, EDAX, FT-IR, TGA, and EPR experiments. The catalyst smoothly catalyzes phenyl selenylation of aryl boronic acids in water and phenyl tellurylation of aryl boronic acids in PEG-600, selectively. Thus a wide variety of unsymmetrical organodiaryl or aryl- heteroaryl selenides and tellurides has been synthesized by this protocol. The catalyst was recycled upto six runs without any appreciable loss of catalytic activity.

Keywords: Phenyl selenylation and tellurylation, aryl boronic acids, solvent selective, Cu@PS-TSC, recyclable.

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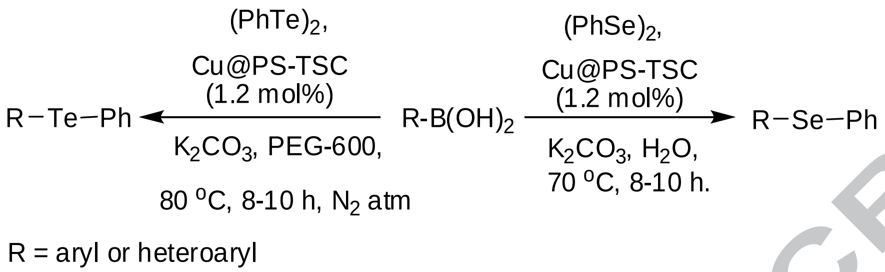
Organochalcogens, especially organoselenides and organotellurides are found as a structural motifs in a wide variety of molecules of interest to biological, pharmaceuticals and material sciences.[1] They have also received considerable attention as synthetic reagents or intermediates in organic synthesis.[2] Thus, several methods have been explored to synthesise organoselenide and organotelluride derivatives.[3]

The reaction of metal selenolate or tellurolate with various electrophiles like organic halides, epoxides, acyl halides, α,β-enones etc. was found to be the most commonly used and general method to introduce the selenium or tellurium moiety into an organic molecule.[4] But the main challenge depends on the synthesis of organoselenides or tellurides from aryl halides by using the common method because of the relatively lower reactivity of aryl-halogen bond.

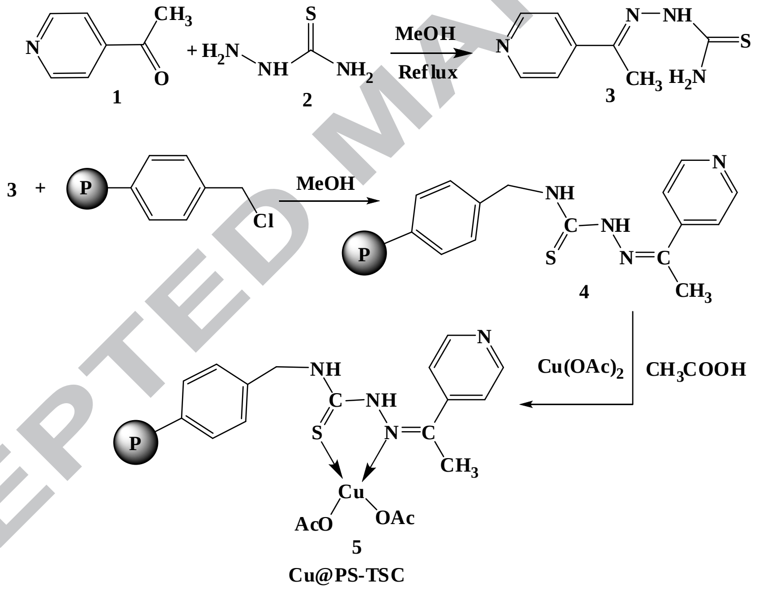
Though several methods have been developed using a transition-metal catalyst like Pd,[5] Ni,[6]and Cu[7] for the synthesis of diaryl sulphides and selenides, but the synthesis of diaryl tellurides is not so successful by these protocols. However, due to the instability and toxicity of PhSeH or PhSeNa those methods are not desirable in the context of green chemistry. To overcome this problem diarylchalcogenides which are relatively stable, less toxic and easily available were employed.[8] L. Wang[9] *et al*. have first employed organoboronic acids instead of aryl halide because of their stability, nontoxicity, easy accessibility and compatibility with various functional groups.[10] After that, the organic boronic acid has become the reagent of choice for the reaction with diaryl dichalcogenides.[11] Several transition metal catalyzed synthesis of organoselenides and tellurides were reported which include CuI,[9,11a] iron,[11b] $InBr_3$,[11c]CuO-NPs,[11d] $CuFe_2O_4$-NPs[11e, 11f] etc. However, most of those methodologies use homogeneous catalysts and hazardous solvent like DMSO which are also not desirable in the context of green chemistry.

Heterogeneous catalysis has gained considerable attention since last decade.[12] With our continued interest on heterogeneous catalysis,[13] we have developed a new heterogeneous copper catalyst Cu@PS-TSC by immobilizing $Cu(OAc)_2$ onto the surface of a thiosemicarbazone functionalized polystyrene which was then applied to catalyze the cross coupling reaction of aryl boronic acids with diphenyldiselenide or diphenylditelluride. A solvent selective methodology for the phenyl selenylation and tellurylation of aryl boronic acids has been carried out in water and PEG-600 respectively to synthesize a library of organo mono selenides and tellurides (Scheme 1).



Scheme 1. Solvent selective phenyl selenylation and tellurylation of aryl boronic acids.

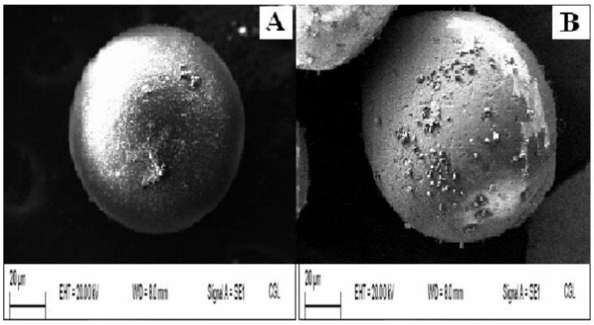
The preparation of the catalyst Cu@PS-TSC is outlined below (scheme 2).



Scheme 2. Synthesis of Cu@PS-TSC catalyst

At first, the 4-acetylpyridine thiosemicarbazone ligand was synthesized according to a reported procedure.[14] A mixture of 4-actetylpyridine **1** (0.10 mol) and thiosemicarbazone **2** (0.10 mol) was refluxed in methanol (100 mL) for 2h. After cooling at room temperature, a white solid was precipitated out. The precipitate was then separated out from the reaction mixture by simple filtration. It was washed with methanol and then recrystallized from warm methanol to furnish pure 4-acetylpyridine thiosemicarbazone ligand **3**. In the next step, the chloromethylated polystyrene (2 g) was added to a methanolic solution of 4-acetylpyridine thiosemicarbazone ligand **3** (1.07 gm in 20 mL). Then it was refluxed for 20 h at 60 ^{0}C. After cooling at room temperature, yellow polystyrene beads were separated out from the reaction mixture which was then washed thoroughly with methanol followed by drying under vacuum. After that, polystyrene-anchored ligand **4** (2 g) was added to acetic acid (20 mL). Copper acetate (0.05 g) in acetic acid (5 mL) was added to the above suspension with constant stirring and then the solution was refluxed for 24 h. After cooling the reaction mixture to room temperature, the separated greenish yellow solid **5** was filtered out, washed thoroughly with methanol and dried under vacuum.

Due to the insolubility of the functionalized polystyrene and Cu@PS-TSC catalyst in all common solvents, their structural investigations were limited only to their physico-chemical properties like SEM, TGA-DTA, IR, and EPR analyses. The copper content was determined by Varian, USA, and AA240 atomic absorption spectrophotometer (AAS). Amount of metal was determined by stripping the bound metal from the support and analysis by using atomic absorption spectrophotometer. Copper content was found in the catalyst is 2.27 wt% of Cu analyzed by AAS. Copper content was remained almost unchanged even after recycling the catalyst for six cycles.The morphology of the catalyst was studied using Scanning Electron Microscope (SEM). The micrographs of the polymer-anchored ligand and Cu@PS-TSC catalyst were obtained from the scanning electron microscope and are presented in figures 1a and 1b respectively. The pure chloromethylated polystyrene beads have smooth surface (not shown). Incorporation of the ligand onto the polystyrene beads introduces a slight roughness on its top layer (Figure. 1a). This roughness is relatively more prominent in the metal complex (Figure 1b) which may be due to the loading of copper metal on polymer anchored ligand.



(a) (b)

Figure 1. FESEM image of (a) ligand **4** and (b) Cu@PS-TSC**5**

The polymer anchored ligand exhibits a broad band around 3300-3450 cm^{-1} due to –NH stretching (secondary amine) vibrations. It also shows peaks at 1155 and 1641 cm^{-1} due to ν(C=S) and ν(C=N) groups. These peaks shifted to lower frequency in the polymer anchored metal complex due to the coordination of metal centre with the ligand. This suggests that the ligand acts as a bidentate chelating agent coordinated through ‘N’ (azomethine) and ‘S’ atom.[15] The pyridine ring vibrations were assigned at 1605, 1571, 1452 and 771 cm^{-1}. These bands are also present in the Cu@PS-TSC complex which means pyridine ring does not participated in the complexation. A medium intensity band observed at 1363 cm^{-1} which suggests the monodentate coordination of the acetate group.

Thermal stability of the complex was investigated using Thermo Gravimetric Analysis (TGA). The polymer anchored ligand is stable in the temperature range 370-380 ^{o}C and polymer anchored copper catalyst is stable upto 400 ^{o}C. It indicates that after complexation with metal the thermal stability of polystyrene increases by 30 ^{o}C.

The EPR (electron paramagnetic resonance) spectra of the fresh and used Cu@PS-TSC catalyst were recorded for the solid sample at room temperature by a JES-FA200 ESR spectrometer (JEOL) (Figure. 2). The X-band EPR spectrum of the fresh and used catalyst show four hyperfine lines resulting from the coupling of the unpaired electron with the nuclear spin of copper(II). In the EPR spectra of fresh catalyst (Figure. 2a), the signal of Cu(II) is centred at g = 2.17 while in the EPR spectra of the used catalyst (Figure. 2a) the signal of Cu(II) is centred at g = 2.11. It is also clear from the spectra of the used catalyst that a slight rhombic distortion took place at the metal centre in the used catalyst.

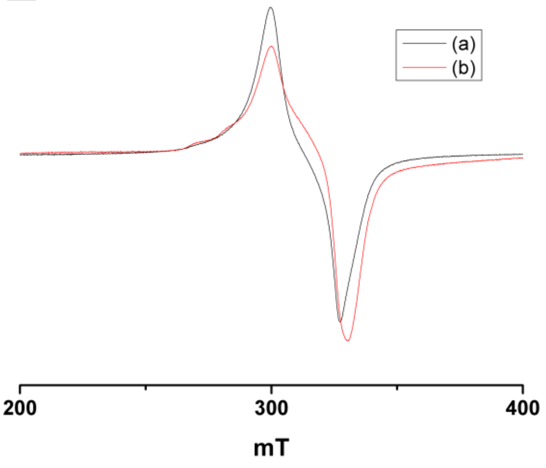
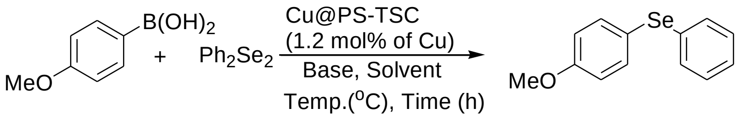


Figure 2.EPR spectra of (a) fresh Cu@PS-TSC and (b) used Cu@PS-TSC.

To optimize the reaction conditions, a series of experiments were carried out with the variation of several parameters like base, solvent, temperature and time for a representative reaction of 4-methoxy phenyl boronic acid and diphenyldiselenide in presence of Cu@PS-TSC (1.2 mol% of Cu) catalyst. The results are tabulated in Table 1.

Table 1. Optimization of reaction conditions[a] for selenylation of aryl boronic acid



Entry	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	Cs_2CO_3	DMF	100	10	92
2	K_2CO_3	DMF	100	10	82
3	K_2CO_3	DMSO	100	10	88
4	K_2CO_3	THF	100	10	-
5	K_2CO_3	H_2O	100	10	92
6	K_2CO_3	H_2O	80	10	92
7	K_2CO_3	H_2O	70	10	92
8	**K_2CO_3**	**H_2O**	**70**	**8**	**92**
9	K_2CO_3	H_2O	60	8	80
10	K_2CO_3	H_2O	70	6	78
11[c]	K_2CO_3	H_2O	70	8	61

[a] Reaction conditions : 4-methoxy phenylboronic acid (1 mmol), diphenyldiselenide(0.5 mmol), K_2CO_3 (1.5 mmol), Cu@PS-TSC (1.2 mol% of Cu), H_2O(4 ml).

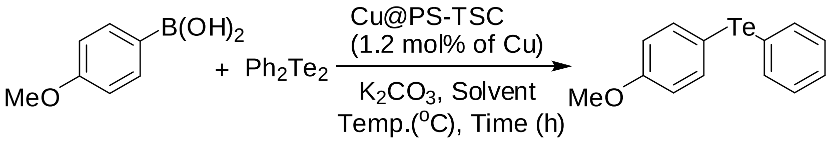
[b] yields refer to those of isolater pure products.

[c] 0.8 mol % of Cu catalyst was used.

Though both Cs_2CO_3 and K_2CO_3 produced similar results in DMF solvent (Table 1, entry 1 and 2), K_2CO_3 has been chosen as the base due to its relative mildness and low cost than Cs_2CO_3. Among various solvent like DMF, DMSO, H_2O and THF, water was found to be the best solvent. Hence, the best result in terms of yield and time was achieved in water at 70 ^oC in the presence of K_2CO_3 (1.5 equiv.) for 8 h (Table 1, entry 8). It was also observed that with the decrease of catalyst loading (0.8 mol% of Cu), corresponding yield of the product also decreases (Table 1, entry 11).

Interestingly, under the similar reaction conditions when 4-methoxy phenyl boronic acid was subjected to react with diphenyl ditelluride, it produced only 25% yield of the corresponding product (Table 2, entry 1). To optimize the reaction conditions for phenyl tellurylation of 4-methoxy phenyl boronic acid several reactions were carried out with the variation of solvent, temperature and time. The results are summarised in Table 2.Though the reaction in DMF and DMSO solvent produced good yields (Table 2, entry 2, 3), PEG-600 was found to be the best solvent for the phenyl tellurylation of 4-methoxy phenyl boronic acid in terms of yield and time at 80 °C (Table 2, entry 9).

Table 2. Optimization of reaction conditions for tellurylation of aryl boronic acids[a]



Entry	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	H_2O	100	10	25
2	DMF	100	10	89
3	DMSO	100	10	88
4	THF	100	10	-
5	Toluene	100	10	-
6	PEG-600	100	10	90
7	PEG-600	80	10	90
8	PEG-600	70	10	78
9	**PEG-600**	**80**	**8**	**90**
10	PEG-600	80	6	73
11[c]	PEG-600	80	8	63

[a] Reaction conditions : 4-methoxy phenylboronic acid (1 mmol), diphenyldiselenide(0.5 mmol), K_2CO_3 (1.5 mmol), Cu@PS-TSC (1.2 mol% of Cu), PEG-600 (4 ml).
[b] yields refer to those of isolater pure products.
[c] 0.8 mol % of Cu catalyst was used.

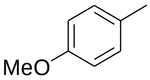
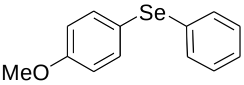
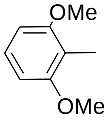
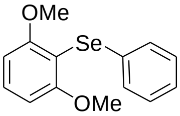
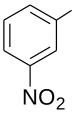
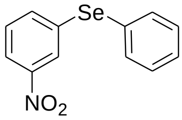
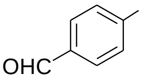
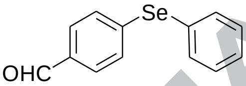
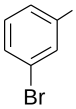
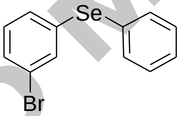
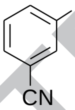
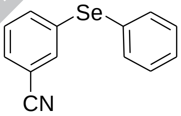
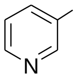
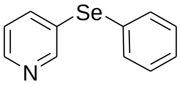
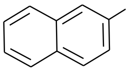
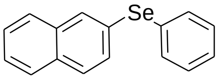
Hence, water and PEG-600 which are both considered as green solvent were chosen for the phenyl selenylation and phenyl tellurylation of aryl boronic acids, respectively. It was also speculated that the two units of both $(PhSe)_2$ and $(PhTe)_2$ were consumed in the reaction.

Thus in a typical reaction procedure, a mixture of aryl boronic acid (1 mmol), diphenyldiselenide (0.5 mmol), K_2CO_3 (1.5 mmol) and Cu@PS-TSC (1.2 mol% of Cu) were heated in water (4 mL) at 70 °C for required period of time (TLC). But for phenyl tellurylation the reaction of aryl boronic acids (1 mmol) with diphenylditelluride (0.5 mmol) was carried out in PEG-600 at 80 °C in presence of K_2CO_3 (1.5 mmol) and Cu@PS-TSC (1.2 mol% of Cu) for a required period of time (TLC).

A wide variety of aryl boronic acids were subjected to react with diphenyldiselenide to produce a library of aryl-phenyl selenides. The results are summarised in Table 3.

Table 3. Cu@PS-TSC catalyzed phenyl selenylation of aryl boronic acids with diphenyldiselenide in water[a]

$$R-B(OH)_2 + (PhSe)_2 \xrightarrow[K_2CO_3,\ H_2O,\ 70\ ^oC]{Cu@PS-TSC\ (1.2\ mol\%\ of\ Cu)} R-Se-Ph$$

Entry	R	Product	Time(h)	Yield[b](%)	Ref.
1.			8	92	11f
2.			10	80	11b
3.			9	88	11f
4.			9	87	11f
5.			8	90	7e
6.			9	91	19
7			9	84	3c
8			9	83	11a

[a] Reaction conditins: boronic acids (1 mmol), diphenyl diselenide (0.5 mmol), K_2CO_3 (1.5 mmol), Cu@PS-TSC (1.2 mol% of Cu), H_2O (4 mL)

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

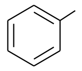
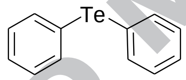
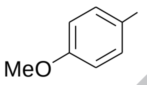
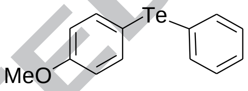
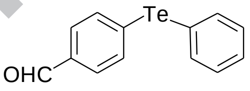
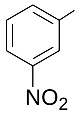
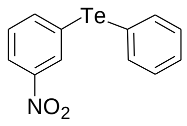
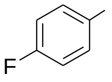
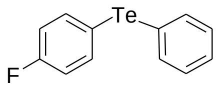
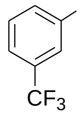
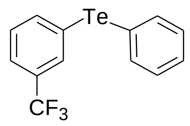
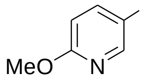
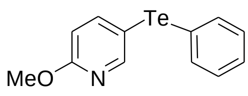
Both electron donating (-OMe) (Table 3, entry 1 and 2) and electron withdrawing (4-NO_2, 4-CHO, 3-Br, 3-CN) (Table 3, entries 3-6) group substituted aryl boronic acids reacted smoothly with diphenyldiselenide to produce the corresponding organoselenides.

Highly sterically hindered 2,6-dimethoxy phenyl boronic acid also underwent phenyl selenylation without any difficulty (Table 3, entry 2). 3-Bromophenyl boronic acid after phenyl selenylation produced (3-bromophenyl)(phenyl) selane (Table 3, entry 5) which can be further converted to various useful molecules by the cross-coupling reaction with an appropriate coupling partner.[16] Heteroaryl substituted boronic acid, *i.e.* 3-pyridyl boronic acid after smooth phenyl selenylation produced 3-(phenylselanyl)pyridine (Table 3, entry 7). 2-Naphthylboronic acid reacted with diphenyldiselenide to produce the corresponding selenide (Table 3, entry 8) which is an analogue of 5-LOX (Lipoxygenase) inhibitor.[17]

Similarly a variety of aryl boronic acids were also subjected to react with diphenyldirelluride under the optimized reaction conditions to obtain a library of aryl-phenyl tellurides. The results are tabulated in Table 4.

Table 4. Cu@PS-TSC catalyzed phenyl tellurylation of aryl boronic acids with diphenylditelluride in PEG-600[a]

$$R{-}B(OH)_2 + (PhTe)_2 \xrightarrow[K_2CO_3,\ \text{PEG-600},\ 80\ ^{o}C]{\text{Cu@PS-TSC (1.2 mol\% of Cu)}} R{-}Te - Ph$$

Entry	R	Product	Time(h)	Yield[b](%)	Ref.
1.			8	87	11g
2.			8	90	11b
3.			9	84	11g
4.			9	89	18
5.			8	90	3g
6.			9	88	-
7			10	84	-

[a] Reaction conditins: boronic acids (1 mmol), diphenyl ditelluride (0.5 mmol), K_2CO_3 (1.5 mmol), Cu@PS-TSC (1.2 mol% of Cu), PEG-600 (4 mL).
[b] Yields refer to those of isolated pure products.

Several functionalities like -OMe, -CHO, -NO_2, -F, -CF_3 were compatible under the mild reaction conditions (Table 4, entries 2-6). Heteroaryl substituted boronic acid, *i.e.* 6-methoxy-3-pyridyl boronic acid reacted easily with diphenylditelluride to furnish the corresponding heteroaryl-phenyl telluride (Table 4, entry 7).

In general the reactions are very clean and high yielding. Several functional groups remain unreacted under the mild reaction conditions. When the reaction was over (TLC), the product was purified from crude reaction mixture by column chromatography. The atomic absorption spectroscopy (AAS) of copper content in the final product did not show the presence of copper which clearly demonstrate that copper was intact to a great extent with the heterogeneous support and there is no significant amount of leaching occurred during the reaction. The catalyst Cu@PS-TSCwas successfully recovered by simple filtration through a cintered glass bed (G-4) and then subsequently washed with ethanol and acetone followed by drying in an oven at 90 °C for 6 h before reuse. The catalyst was successfully recycled upto 6th run without any appreciable loss of catalytic activity for both phenyl selenylation and phenyl tellurylation of 4-methoxy phenyl boronic acid (Figure. 3).

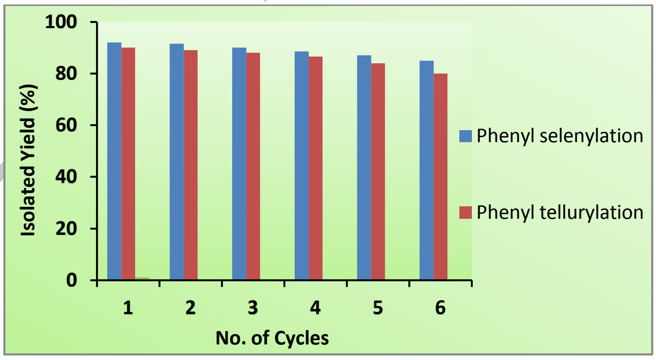


Figure 3. Recyclability chart of Cu@PS-TSC catalyst

In conclusion, we have developed a solvent selective methodology for the phenyl selenylation and phenyl tellurylation of aryl boronic acids catalyzed by a newly synthesized heterogeneous Cu@PS-TSC catalyst to furnish a wide range of organo mono selenides and tellurides. The notable advantages offered by this protocol are the use of green solvents such as water for phenyl selenylation and PEG-600 for phenyl tellurylation, scope for the synthesis of organoselenides and tellurides, simplicity in operation, general applicability, mild reaction conditions, compatibility of a wide range of functionalities including the pyridine moiety, use of a new synthesized recyclable catalyst, high yield of product using a low catalyst loading

(1.2 mol% of Cu) which implies high Turn Over Number (TON) of the catalyst, utilization of both the unit of $(PhSe)_2$ or $(PhTe)_2$ in the reaction which implies that the reaction is atom economic, high purity of the product etc. These advantages make this procedure green and cost effective. To the best of our knowledge, we are not aware of such kind of solvent selective phenyl selenylation and tellurylation of aryl boronic acids with a greener perspective. Hence we believe that this methodology will be an important addition to the existing methods for the synthesis of organoselenides and tellurides with respect to green chemistry.

Acknowledgements

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Supplementary Material

Representative experimental procedures, characterization data, copies of ^{1}H NMR and ^{13}C NMR spectra of all products listed in Table 3 and 4 are given in this section.

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Solvent selective phenyl selenylation and phenyl tellurylation of aryl boronic acids catalyzed by Cu(II) grafted functionalized polystyrene

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Research Highlights

- A new polymer supported copper(II) catalyst has been synthesized and characterized.
- Solvent selective Phenyl selenylation and phenyl tellurylation of aryl boronic acids.
- Phenyl selenylation in H_2O and Phenyl tellurylation in PEG-600 solvent.
- Hazardous organic solvents throughout the reaction were avoided.
- This catalyst can be recycled upto six times.

Graphical abstract

Solvent selective phenyl selenylation and phenyl tellurylation of aryl boronic acids catalyzed by Cu(II) grafted functionalized polystyrene

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