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FULL PAPER

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Nano $CoCuFe_2O_4$-catalyzed coupling reaction of arylboronic acid with amines and thiols: An atom-economic and ligand-free route to access unsymmetrical amines and sulfides

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An efficient protocol was developed for the nano $CoCuFe_2O_4$-catalyzed C-N and C-S bond formation. By this catalytic system, both amine and sulfide-based structural motifs were formed efficiently in aryl halide-free route. The amination reaction of phenyl boronic acid with various types of amines was conducted under ligand-free conditions, in ethanol as a green solvent at 60°C. Unsymmetrical diaryl/aryl alkyl sulfide synthesis via the coupling reaction of arylboronic acids with thiols was also conducted. The nano cobalt-copper ferrite was used as a heterogenous efficient, inexpensive, magnetically separable and recyclable catalyst that can be used for several cycles.

KEYWORDS
amination, boronic acid, $CoCuFe_2O_4$, ligand-free, sulfidation

1 | INTRODUCTION

The carbon–heteroatom bond forming reaction is one of the most important reactions in organic synthesis, pharmaceutical, dye, agrochemical and biomolecules.[1] Therefore, improvement of efficient methodologies for generating carbon–heteroatom bonds received considerable attention.

The first metal-based synthesis of amines was reported by Ullmann and Goldberg over 100 years ago.[2,3] In 1983, Migita and his co-workers synthesized aniline derivatives via tributyltin amide and aryl bromides catalyzed with palladium and phosphine ligand.[4] Then, in the 2000s, Buchwald and Hartwig used palladium and copper complexes to activate aryl halides to generate C-N bond in the presence of amine as a nucleophile.[5,6] However, these methods suffer from harsh reaction conditions, such as requiring a high temperature (110°C), which makes them incompatible for a range of functional groups. The high cost and toxicity of palladium complexes[7] have stimulated the search for alternative affordable transition metal catalysts, such as nickel,[8] copper,[9] iron,[10] cobalt[11] and also metal-free cross-coupling catalysis. Also, employing homogeneous catalysts in those processes makes them inefficient in pharmaceutical synthesis and drug discovery approaches as a trace amount of remaining metal in products has negative effects on health.[12]

Concerning facile catalyst recycling, magnetic catalysts rank among the available techniques, as in this way the application of an external magnet readily separates the catalyst from the reaction media and eliminates the need for filtration.

Recently, in the realm of cross-coupling reactions, magnetic metal oxide nanoparticles with spinel structure have attracted considerable attention.[13] In fact, the synergetic effect among existing transition metals in these systems could enhance their catalytic activity.[14,15]

It is worth noting that transition metal-free amination reaction was also carried out, but the rates of conversions and selectivity were not as high as metal-catalyzed ones.[16]

In the case of thioether synthesis, the strong coordinative feature of sulfur-containing compounds leads to some difficulties in C-S bond formation as sulfur species rapidly and irreversibly deactivate the catalyst. The Chan–Lam reaction is a valuable alternative to traditional cross-coupling for construction of carbon-heteroatom bonds due to the mildness of this reaction. The first C-S bond formation through the Chan–Lam reaction was reported by Guy *et al.*, in which boronic acids reacted with alkyl thiols in the presence of stoichiometric Cu $(OAc)_2$.[17]

Numerous modifications of this method have been published thereafter.[18,19] However, the development of mild and cost-effective catalytic procedures for N-arylation of amines and S-arylation of thiols still remains an active research area. Aryl halide, aryllead, arylbismuth, arylborane and arylsilane compounds are used as coupling components for arylation reactions.[20–24] Of these aryl surrogates, arylboronates are commercially available, non-toxic, easily handled, and stable under air and moisture.

In this direction, we wish to report an inexpensive strategy for amination and sulfidation coupling reactions. Co and Cu are abundant, inexpensive and a variety of their salts are commercially available. Using our catalytic system, the reaction conditions can be improved and it accelerates the reaction without using expensive transition metals and ligands such as palladium and phosphine, respectively.

2 | RESULTS AND DISCUSSION

2.1 | Catalyst synthesis

$CoCuFe_2O_4$ nanoparticles were prepared using the co-precipitation method according to our previously reported procedure.[25] We have recently applied $CoCuFe_2O_4$ in the Sonogashira coupling reaction.[25] Encouraged by the good performance of cobalt-copper ferrite on C-C bond formation, we investigated its application in C-heteroatom bond formation via the Chan–Lam coupling reaction. Apart from the previously reported analysis for the characterization of our catalyst, the exact characterization of heterogeneous catalysts and a better understanding of factors affecting catalytic properties are not so simple. By means of X-ray photoelectron spectroscopy (XPS) analysis as a surface-sensitive technique, we are able to partly overcome this challenge. Therefore, we determined the cation distribution and chemical state of the surface of our samples by XPS analysis. A wide scan of the samples was first realized (0–1200 eV) to detect all the species in the sample (Figure S1). The XPS spectrum of $CoCuFe_2O_4$ possesses four peaks centered at 529.8, 709.8, 779.8 and 932.8 eV, corresponding to O 1s, Fe 2p, Co 2p and Cu 2p, respectively.[26,27] As shown in Figure S2, the O 1s XPS signals showed three peaks at 529.8, 531.7 and 533.8 eV. The main peak at 529.8 eV is attributed to the contribution of the crystal lattice oxygen, which is a characteristic of the surface spinel. However, the appearance of shoulder peaks at higher binding energy is not clear. In fact, the exact assignment of them is rather complex due to a number of factors, such as surface defects, contaminants, impurities or chemisorbed oxygen species.

Concerning the Fe 2p spectra, in Figure S3 one can see the binding energy at 709.8 eV is ascribed to Fe^{3+} ions in octahedral sites, while the binding energy at 713.2 eV is caused by Fe^{3+} ions in tetrahedral sites.

The cobalt cations are present as Co^{2+} cations. The existence of two peaks with binding energies of 779.8 and 781.4 eV arises from the random distribution of the Co^{2+} within the tetrahedral and octahedral layers of the ferrite structure, respectively (Figure 1).

For copper, the XPS analysis revealed that copper species with 2+ valance are present at the surface of the catalyst. Cu^{2+} was found to occupy both the tetrahedral and octahedral sites in spinel. However, the octahedrally coordinated surface Cu species is predominant. The peak at 932.8 eV is attributed to octahedral Cu^{2+}, and the peak at 934.8 eV to tetrahedral Cu^{2+}. Satellite signals located on the higher binding energies (937.3, 940.4, 943.5, 945.3 eV) are sensitive to changes in the coordination environment of Cu^{2+} ions (Figure 2).

Binding energies and transitions of Cu 2P3/2, Co 2P3/2 and Fe 2P3/2 are summarized in Table S1; assignments were made by comparison with the values reported in the literature.[26,27] Apart from previously reported analyses, such as atomic absorption spectroscopy,

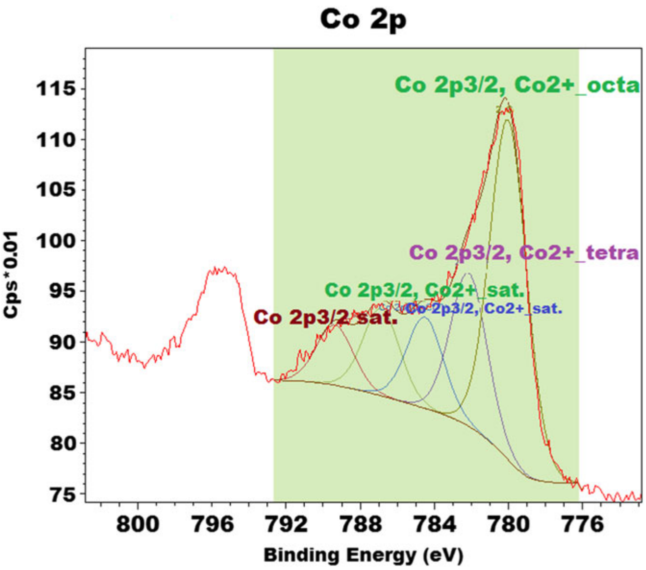


FIGURE 1 X-ray photoelectron spectroscopy (XPS) spectrum for Co 2p of $CoCuFe_2O_4$

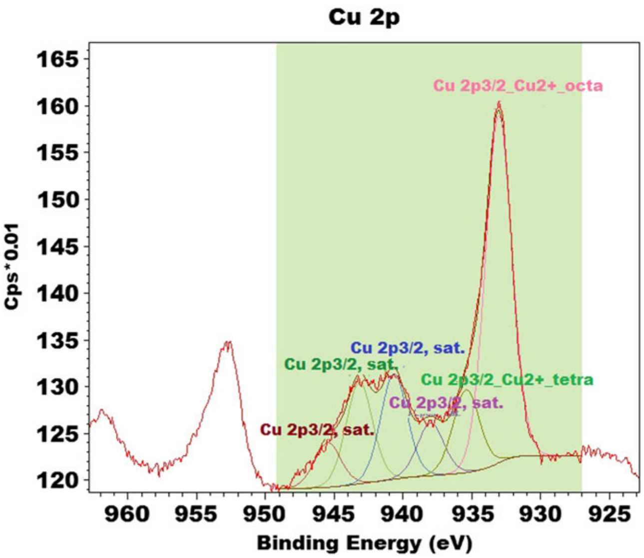


FIGURE 2 X-ray photoelectron spectroscopy (XPS) spectrum for Cu 2p of $CoCuFe_2O_4$

scanning electron microscopy, vibrating-sample magnetometry, X-ray diffraction, energy-dispersive X-ray spectrometry, transmission electron microscopy and Fourier transform-infrared analysis[25] (see Supporting Information), these XPS results further confirmed the formation of cobalt-copper ferrite.

Our catalytic system, in comparison with previously reported palladium or copper-based catalysts,[28,29] not only has low cost but is also readily prepared in a few steps from available starting materials and can be removed easily from the reaction media due to its ferromagnetic nature. This is a very important factor for creating non-polluting catalysts, because the trace amount of metal contamination could have undesired effects on human-life-related products.

Our research has focused on the reduction of costs by the creation of highly active catalysts, and on the reduction of waste by developing a halide-free amination/sulfidation reaction based on the use of arylboronic acids as arylating agents. Therefore, due to the employment of arylboronic acids as an arylating surrogate, atom economy was improved compared with the systems that used aryl halides. From the perspective of process development, there is a strong demand to simplify reactions as much as possible. In this respect, we report the catalytic system that possesses no ligands and is still capable of effectively catalyzing the construction of the carbon-heteroatom bond. In fact, the presence of ligands can be a nuisance, particularly at high catalyst loadings, as they are often hard to separate from the product.

We set out a route by which disadvantages associated with the classical cross-coupling reactions, such as the need for presynthesizing of starting materials and consequently reducing atom and step economy, were left behind. Compared with conventional approaches, this method is more atom-economic because of using a sub-stoichiometric amount of catalyst, whereas in the conventional methods large quantities of residues such as halide salt are produced and a large amount of transition metal source is wasted.[30]

2.2 | Catalytic activity

Our study initially focused on a typical reaction of phenyboronic acid and aniline as model substrates. Initially, the results of base screening showed the desired product could be obtained in both organic and inorganic bases. However, the high yield of the product was isolated in the presence of KOH, and other bases such as K_2CO_3, KOAc, KOtBu, $NaHCO_3$, DABCO and Et_3N were not effective (Table 1, entry 4). Next, we examined the impact of solvent on amination reactions. After a survey of several solvents, we found that EtOH was an excellent solvent for this transformation, which paves the way to the green chemistry. Strong polar solvents such as DMF and DMSO were also used resulting in obtaining the desired product in 80% and 30% yields, respectively. Reducing the catalyst loading resulted in a decreased yield of the product. No anticipated product was observed in the absence of catalyst (Table 1, entry 20). Exploring the effect of temperature on the reaction showed that low yields were obtained when the temperature was changed to room temperature or 40°C, and 60°C was chosen as an optimum reaction temperature.

After the establishment of the optimized conditions, this protocol was applied to access a variety of arylamines (Table 2). Phenylboronic acids with an electron-releasing group (OCH_3) afforded slightly better yields than did those with electron-withdrawing groups (NO_2).

After achieving excellent results with aliphatic acyclic amines such as diethyl amine, dibutylamine, benzylamine, propylamine and *N,N* dicyclohexyl amine, we further applied this catalytic system for the N-arylation of aromatic and cyclic aliphatic amines. In the case of aromatic amines, those including electron donor substituents afforded the corresponding arylated products in higher yields compared with amine-bearing electron-withdrawing groups. The aliphatic boronic acid (but-1-yn-1-ylboronic acid) was also examined and the corresponding product obtained in moderate yield (1s). Pyridin-3-ylboronic acid was chosen as a heteroaromatic boronic acid provided the corresponding products 3-(1H-imidazol-1-yl) pyridine in low yield (1t).

One of the most important issues associated with the heterogeneous catalyst is its recyclability. In this regard, the yield of the model product (the reaction of aniline with phenylboronic acid) in the presence of the fresh

TABLE 1 Optimization of reaction conditions on amination reaction of phenylboronic acid with aniline in the presence of catalyst[a]

Entry	Base	Solvent	Catalyst (mol%)	Temperature (°C)	Yield[b] (%)
1	Et_3N	CH_3OH	2.5	60	50
2	DABCO	CH_3OH	2.5	60	45
3	K_2CO_3	CH_3OH	2.5	60	54
4	KOH	CH_3OH	2.5	60	70
5	KOAc	CH_3OH	2.5	60	60
6	$NaHCO_3$	CH_3OH	2.5	60	52
7	KOtBu	CH_3OH	2.5	60	57
8	KOH	H_2O	2.5	60	20
9	KOH	EtOH	2.5	60	82
10	KOH	CH_3CN	2.5	60	32
11	KOH	CH_2Cl_2	2.5	60	78
12	KOH	Toluene	2.5	60	21
13	KOH	1,4 Dioxane	2.5	60	25
14	KOH	DMSO	2.5	60	30
15	KOH	DMF	2.5	60	80
16	KOH	EtOH	5	60	88
17	KOH	EtOH	5	40	30
18	KOH	EtOH	5	R.T.	N.R.
19	KOH	EtOH	5	80	89
20	KOH	EtOH	–	60	N.R.

N.R., No Reaction; R.T., Room Temperature.

[a] Reaction conditions: phenylboronic acid (0.1 mmol), aniline (0.2 mmol), base (0.15 mmol), solvent (1 ml), 5 h.

[b] Isolated yields.

$CoCuFe_2O_4$ was compared with those of reused catalysts. In this line, the recovered catalyst was washed with EtOH, dried and reused for consecutive reaction runs. The results showed that the catalyst could be recovered and reused for five reaction runs with a slight loss of the catalytic activity for the reaction of aniline and phenylboronic acid under optimized reaction conditions (Figure S10).

Encouraged by obtaining outstanding results in the amination reaction, we next tested the efficiency of catalyst for the coupling reaction of thiols with aryl boronic acids. The optimal reaction conditions were elaborated in the reaction of phenylboronic acid and thiophenol. The data from the optimization reactions are shown in Table 3. First, various solvents were tested. Running the reaction in ethanol afforded the desired product in poor 20% yield (Table 3, entry 6), and the use of DMSO, DCE, THF and dioxane as solvents afforded product in small amounts. However, we noted that a good yield (83%) of the desired product could be obtained in DMF.

The study was further carried out using different bases, including organic and traditional inorganic ones such as NaOH, K_2CO_3, KOtBu, KOAc, $NaHCO_3$ and Cs_2CO_3. All proved inferior to n-Bu_4NOH (40%, aq.) in terms of yield.

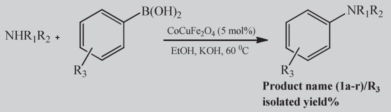
We tried to accelerate the rate of coupling by raising reaction temperature. However, through enhancing the reaction temperature up to 120°C no perceptible increase in the reaction yield was observed.

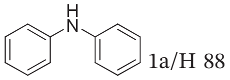
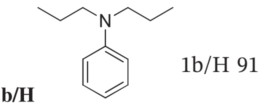
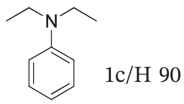
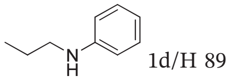
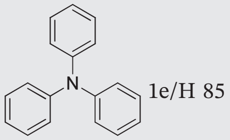
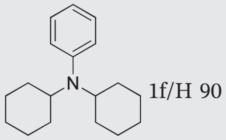
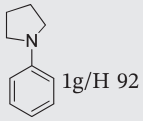
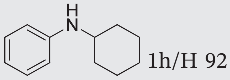
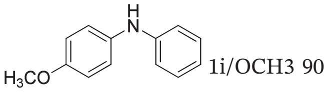
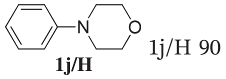
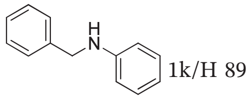
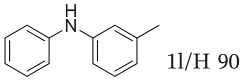
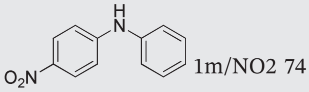
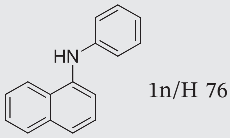
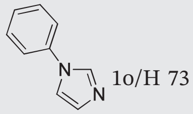
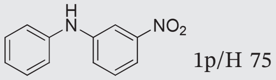
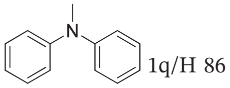
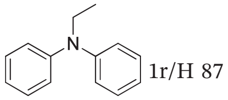
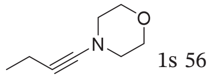
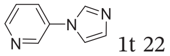
As a final step, the dependence of the results on catalyst loading was tested. Reducing the catalyst amount from 5 mol% to 2.5 mol% led to a significant drop in yield from 83% to 56%. A further increase of the catalyst amount to 10 mol% could not improve the result to a better extent. The reaction was shut down in the absence of catalyst.

Armed with the optimum reaction conditions, the generality of this protocol was examined by using various substrates with different electronic properties. As shown in Table 4, the reaction can be conducted using both linear and aromatic sulfides.

The reactions of substituted thiophenols bearing both electron-donating and electron-withdrawing groups with phenylboronic acid proceeded smoothly leading to the desired products in high yields. The results also indicated that the electronic effect of substituents on the benzene

TABLE 2 N-arylation of amines with phenylboronic acids[a]



 **1a/H** **88**	 **1b/H** **91**	 **1c/H** **90**	 **1d/H** **89**
 **1e/H** **85**	 **1f/H** **90**	 **1g/H** **92**	 **1h/H** **92**
 **1i/OCH3** **90**	 **1j/H** **90**	 **1k/H** **89**	 **1l/H** **90**
 **1m/NO2** **74**	 **1n/H** **76**	 **1o/H** **73**	 **1p/H** **75**
 **1q/H** **86**	 **1r/H** **87**	 **1s** **56**	 **1t** **22**

[a]Reaction conditions: arylboronic acid (0.1 mmol), amine (0.2 mmol), KOH (0.15 mmol), EtOH(1 ml), 60°C, 5 h.

ring of arylboronic acid has limited influence on this heterogeneous catalyzed Chan–Lam coupling reaction. More strongly electron-donating (methoxy) or electron-withdrawing (nitro) substitutions do not significantly affect the reaction overall yields. The coupling of cyclohexylboronic acid as an aliphatic boronic acid with thiophenol only gave a trace amount of product (2m). However, the reaction of 3-thiopheneboronic acid with thiophenol provided the corresponding product in moderate yield (2n).

In continuation, the separation of $CoCuFe_2O_4$ nanoparticles from the reaction mixture was studied using an external magnetic rod. We have studied the possibility of catalyst recycling from the reaction of thiophenol with phenylboronic acid under optimized reaction conditions. After each reaction cycle, the catalyst was separated by an external magnet rod, rinsed with ethanol several times, dried, and reused for the subsequent reaction for five consecutive runs (Figure S11).

Considering the fact that the reaction could not proceed without $CoCuFe_2O_4$ and along with recent published work led us to propose a mechanism for the Chan–Lam coupling reaction.[31] As depicted in Scheme 1, the reaction pathway starts with transmetallation of arylboronic acid, which is in equilibrium with the boronate ester,[32] to afford intermediate A and releasing boric acid. This step is a turnover-limiting step. In fact, the nanoparticles may facilitate the coupling reactions due to the easier transfer of electrons and the higher surface area in comparison to bulk metal salts. Then, RX^- (where $X = S, N$) derived from RXH and base coordinates to intermediate A to form intermediate B. Finally, intermediate B produced the desired product and completed the catalytic cycle. In support of this mechanistic speculation, no disulfide was observed as an intermediate during the reaction followed by GC.

By this catalytic system, desired products were formed with yields comparable with the previous catalytic system. Another advantage is that reactions required approximately shorter times to be completed, indicating better activity of the $CoCuFe_2O_4$ nanoparticles. In addition, this spinel catalyst is cheaper and more effective than previous palladium-based catalytic systems and their raw materials are available.

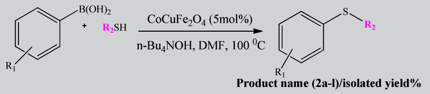
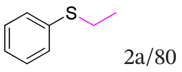
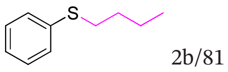
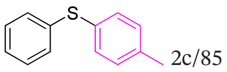
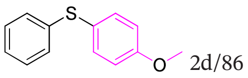
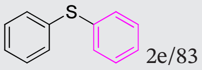
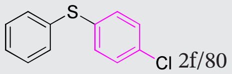
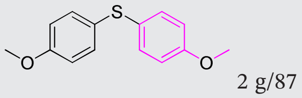
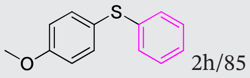
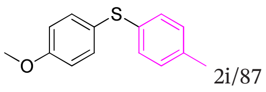
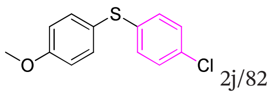
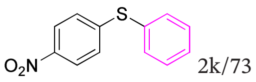
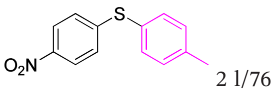
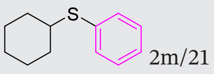
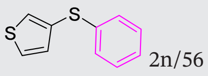
TABLE 3 Optimization of reaction conditions on the Chan–Lam reaction of phenylboronic acid with thiophenol in the presence of catalyst[a]

Entry	Solvent	Base	Temperature (°C)	Catalyst (mol%)	Isolated yield (%)
1	DMSO	NaOH	100	5	69
2	DMF	NaOH	100	5	72
3	DCE	NaOH	Reflux	5	45
4	THF	NaOH	Reflux	5	40
5	Dioxane	NaOH	100	5	32
6	EtOH	NaOH	Reflux	5	20
7	DMF	K_2CO_3	100	5	50
8	DMF	KOtBu	100	5	53
9	DMF	KOAc	100	5	51
10	DMF	$NaHCO_3$	100	5	49
11	DMF	Cs_2CO_3	100	5	60
12	DMF	Et_3N	100	5	70
13	DMF	Pyridine	100	5	74
14	DMF	*n*-Bu_4NOH (40% aq.)	100	5	83
15	DMF	*n*-Bu_4NOH (40% aq.)	80	5	58
16	DMF	*n*-Bu_4NOH (40% aq.)	120	5	84
17	DMF	*n*-Bu_4NOH (40% aq.)	100	2.5	56
18	DMF	*n*-Bu_4NOH (40% aq.)	100	10	84
19	DMF	*n*-Bu_4NOH (40% aq.)	100	–	N.R.

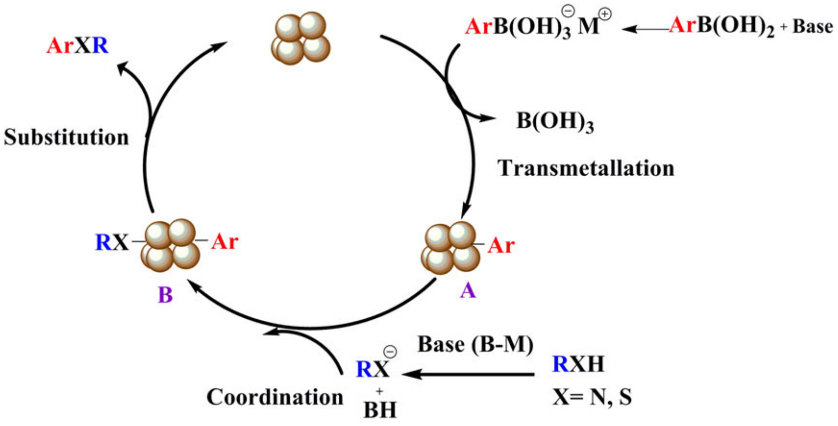
N.R., No Reaction.

[a] Reaction conditions: PhB $(OH)_2$ (0.5 mmol), thiophenol (0.7 mmol), base (1.5 mmol), solvent (1 ml), 10 h.

TABLE 4 Cobalt-copper ferrite nanoparticles catalyzed thioetherification of different sulfides and arylboronic acids[a]

			
 **2a/80**	 **2b/81**	 **2c/85**	 **2d/86**
 **2e/83**	 **2f/80**	 **2g/87**	 **2h/85**
 **2i/87**	 **2j/82**	 **2k/73**	 **2l/76**
 **2m/21**	 **2n/56**		

[a] Reaction conditions: arylboronic acid (0.5 mmol), sulfide (0.7 mmol), *n*-Bu_4NOH (0.15 mmol), DMF (1 ml), 100°C, 10 h.



SCHEME 1 Proposed mechanism for Chan–Lam cross-coupling reaction catalyzed by cobalt-copper ferrite

3 | CONCLUSION

In summary, this newly developed method demonstrates a new alternative to the existing method that is cost effective and an atom-economic approach to C-heteroatom bond formation. This report introduces a mild, green and practical method for preparation of N-arylamines via the coupling reaction of aryl boronic acid with diversity of amines including primary and secondary ones in high yields. The catalyst was also successfully applied for unsymmetrical sulfides through coupling reaction of thiols with phenyl boronic acid as an arylating surrogate.

Using inexpensive catalyst and user-friendly starting materials have made these methods valuable for C-N and C-S bond formation. The magnetic nature of the catalyst enables it to be easily removed from the reaction mixture by an external magnet, which prevails the issues associated with the filtering separation method.

4 | EXPERIMENTAL

4.1 | Reagents and analyses

All materials used are commercially available, and were purchased from Merck and used without any additional purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker (Avance DRX-500) spectrometer using $CDCl_3$ or DMSO-d_6 as solvent at room temperature. Chemical shifts δ were reported in ppm relative to tetramethylsilane as an internal standard. XPS analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultrahigh vacuum.

4.2 | Synthesis of $CoCuFe_2O_4$

The solutions of iron chloride ($FeCl_3{\cdot}6H_2O$; 100 ml, 0.1 M), copper chloride ($CuCl_2{\cdot}2H_2O$; 100 ml, 0.02 M) and cobalt chloride ($CoCl_2{\cdot}6H_2O$; 100 ml, 0.03 M) were prepared separately and mixed together. The solution was stirred for 1 h. Then, in order for pH to reach 11, a solution of NaOH (0.3 M) was added slowly to the flask. Finally, oleic acid (3 drops) was added to the solution as a surfactant to prevent the aggregation and agglomeration of the nanoparticles. Then, the suspension was vigorously stirred using a magnetic stirring bar at 60°C for 2 h. After complete precipitation, the residue was washed with double-distilled water (3 × 25 ml) and dried in an oven at 90°C overnight; then it was calcinated at 600°C for 4 h. The final product is a black powder showing magnetic properties.

4.3 | General procedure for amination reaction

A glass tube was charged with phenylboronic acid (1 mmol), amine (1.2 mmol), KOH (1.5 mmol), EtOH (1 ml) and $CoCuFe_2O_4$ (5 mol%). The reaction mixture was stirred at 60°C until the completion of the reaction, which was monitored by thin-layer chromatography (TLC; EtOAc/*n*-hexane, 25:75). In each case, after completion, the mixture was diluted with ethyl acetate and water. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 75:25). All products were known compounds and were identified by comparison of their ^1H NMR spectra with those of authentic samples.[33]

4.4 | General procedure for sulfidation reaction

A mixture of phenylboronic acid (0.5 mmol), thiol (0.7 mmol), *n*-Bu_4NOH (1.5 mmol) and $CoCuFe_2O_4$ (5 mol%) was added to DMF (1 ml) in a round-bottomed flask equipped with magnet and condenser. The reaction mixture was stirred at 100°C until the completion of the reaction, which was monitored by TLC (EtOAc/*n*-hexane, 25:75). In each case, after completion, the mixture was diluted with ethyl acetate and water. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure using a rotary evaporator. The residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 75:25). All products were known compounds and were identified by comparison of their ^1H NMR spectra with those of authentic samples.[34,35]

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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