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Fe_3O_4 nanoparticle-supported Cu(II)-β-cyclodextrin complex as a magnetically recoverable and reusable catalyst for the synthesis of symmetrical biaryls and 1,2,3-triazoles from aryl boronic acids†

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We report here on the preparation of an efficient, easily recoverable and reusable Fe_3O_4 magnetic nanoparticle-supported Cu(II)-β-cyclodextrin complex catalyst for the synthesis of symmetrical biaryls and 1,2,3-triazoles from arylboronic acids. The presented Fe_3O_4 magnetic nanoparticle-supported Cu(II)-β-cyclodextrin complex catalyst was characterized by TEM, XRD, VSM, TGA, and FT-IR spectrometer. By using the catalyst, we have developed an efficient protocol for the homocoupling of aryl boronic acids for the synthesis of biaryls. The catalyst is also active in the synthesis of 1,2,3-triazoles *via* a one-pot reaction of an arylboronic acid with sodium azide in water followed by a click cyclization reaction with an alkyne at room temperature in air without any additives. The reusability of the prepared nanocatalyst was successfully examined four times with only a very slight loss of catalytic activity.

Introduction

During the past decade, a great deal of attention has been paid to developing greener chemical processes and synthetic methods.[1] Catalysts bound to inorganic solids are widely used for organic transformations due to environmental and economical considerations.[2] Nanoparticles supported on a metal oxide as an inorganic solid, in particular magnetic nanoparticles (MNPs), have been extensively studied in the field of chemical catalysis, environmental protection, sensors, magnetic storage media, and clinical diagnosis treatments.[3] MNPs have great potential in view of the their recovery, since the magnetic separation of MNPs from the reaction mixture with an external magnet is simpler and more efficient than conventional separation with filtration or centrifugation. On the other hand, MNPs are accessible from inexpensive materials and can be easily supported by organic and inorganic materials.[4] Recently, MNP-supported-copper ions have been used extensively in organic transformations.[5,6]

Since the first copper-mediated coupling reaction of aryl halides performed by Ullmann over a century ago,[7] considerable efforts have led to variety of methods and catalysts for the synthesis of symmetrical biaryls.[8] The copper-mediated homocoupling of aryl boronic acids proved to be a valuable method to obtain symmetrical biaryls due to its compatibility with a variety of functional groups, stability and the lower toxicity of the boronic acids than other organometallic reagents.[9] Copper-mediated 1,3-dipolar cycloaddition (click reaction) of organic azides with alkynes to give 1,2,3-triazoles has also received considerable attention because of their useful widespread applications in the fields of material science and molecular structure design.[10] One-pot synthesis of 1,2,3-triazoles *via* the *in situ* generation of aryl azides from aryl boronic acids in the presence of the alkyne using copper-catalysts minimizes the hazards derived from their isolation and handling.[11]

With the increasing demand for environmentally friendly methods, recently we have found that the Cu(II)-β-cyclodextrin complex is an efficient nanocatalyst for the homocoupling and one-pot synthesis of 1,2,3-triazoles from arylboronic acids under base-free homogenous conditions.[12] Cu(II)-β-cyclodextrin complex is a binuclear complex with a good stability constant that can be prepared readily by the addition of a copper sulfate solution to a mixture of β-cyclodextrin in a sodium hydroxide solution.[13] This readily available binuclear supramolecular copper complex is already known, but for the first time we have employed it as a nanocatalyst in organic transformations.[12] Although homogeneous copper catalysts have many advantages, such as a high turnover number, good

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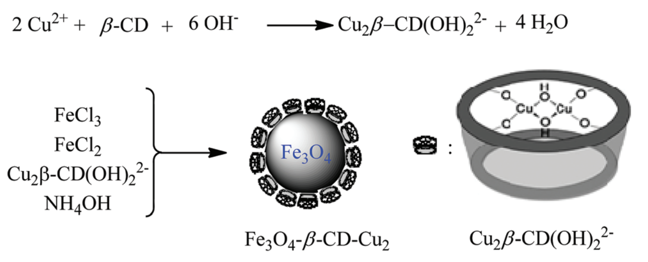
activity and selectivity, and are widely used in a variety of industries, separation of the soluble catalyst from the product and reaction medium remains difficult. Recovery of the copper catalyst and its reuse are two important features for the synthesis of symmetrical biaryls and 1,2,3-triazoles from arylboronic acids. Herein, we report on the preparation and characterization of a Fe_3O_4 magnetic nanoparticle-supported Cu(II)-β-cyclodextrin complex (Fe_3O_4-β-CD-Cu_2). In addition we describe its utility for the synthesis of symmetrical biaryls and 1,2,3-triazoles from arylboronic acids.

Results and discussion

The magnetic nanoparticle-supported Cu(II)-β-cyclodextrin complex (Fe_3O_4-β-CD-Cu_2) was prepared by a simple one-pot co-precipitation of a mixture of iron precursors (Fe^{2+} and Fe^{3+}) and the Cu(II)-β-cyclodextrin complex (prepared according to our previously reported method[12]) in the reaction medium (Scheme 1). The morphology and structure of the prepared Fe_3O_4-β-CD-Cu_2 nanoparticles were characterized by TEM, TGA, XRD and FT-IR analyses, which confirmed the successful preparation of the supported Fe_3O_4 nanoparticles.

Fig. 1 shows the FT-IR spectra of the unsupported Fe_3O_4, Cu(II)-β-cyclodextrin, and Fe_3O_4-β-CD-Cu_2 in the 400–4000 cm^{-1} wave number range. It shows that the adsorption band of the Fe–O bonds in the tetrahedral sites is 581 cm^{-1}, which is shifted to 634 cm^{-1} after being supported with Cu(II)-β-cyclodextrin. The broad band at 3000–3500 cm^{-1} is due to the hydroxy stretching vibration. The spectrum of Fe_3O_4-β-CD-Cu_2 shows the peaks at the 800–1620 cm^{-1} range, which correspond to the characteristic vibrations of β-cyclodextrin. The peak at 1030 cm^{-1} corresponds to the antisymmetric C–O–C vibrations. The intense peak at 1620 cm^{-1} may be assigned to the deformation vibrations of water molecules trapped into the Fe_3O_4 colloidal particles.[14] The assignments are concordant with the Keiser *et al.*[15] and Racuciu *et al.*[14] reports on Fe_3O_4-supported β-cyclodextrin. Therefore, it can be concluded that Cu(II)-β-cyclodextrin has been supported successfully on the surface of Fe_3O_4 nanoparticles. The adsorption and coating of Cu(II)-β-cyclodextrin onto nano-size crystal planes of the Fe_3O_4 nanoparticles was brought about by the strong hydrogen bonding of Cu(II)-β-cyclodextrin, with a multiple hydroxyl group, and the hydroxide groups of the Fe_3O_4 nanoparticles.[16]



Scheme 1 Preparation of the Fe_3O_4 magnetic nanoparticle-supported Cu(II)-β-cyclodextrin complex catalyst.

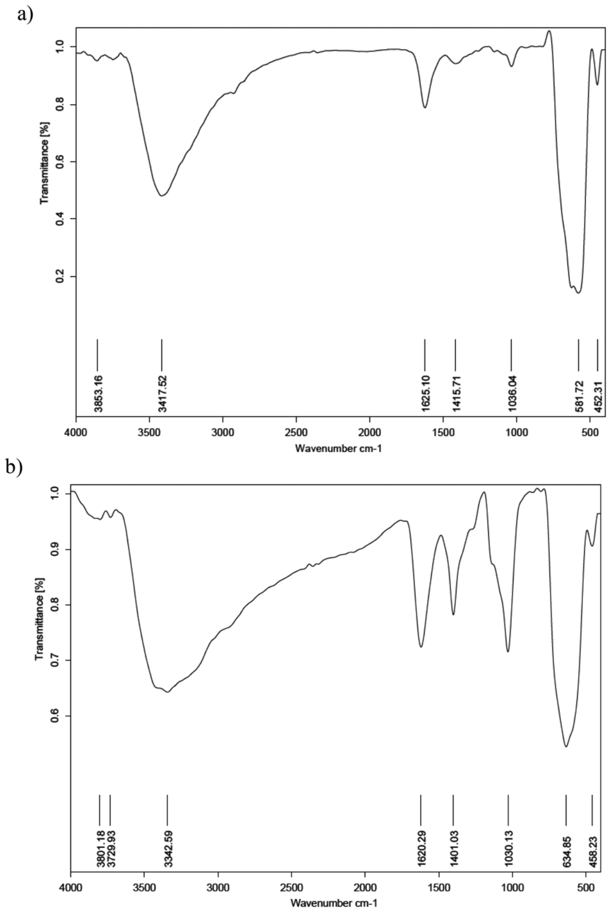


Fig. 1 FT-IR spectrum of (a) Fe_3O_4 and (b) Fe_3O_4-supported Cu(II)-β-cyclodextrin.

The amount of the Cu(II)-β-cyclodextrin complex supported on the surface of the Fe_3O_4 was estimated by thermogravimetric analysis (TGA) of Fe_3O_4-β-CD-Cu_2. As shown in Fig. 2, the TGA curve of the Fe_3O_4-supported Cu(II)-β-cyclodextrin shows a weight loss of 3.69% below 160 °C, which is due to the loss of the adsorbed water in the sample. The mass loss of about 8.33% by weight in the range of 160–340 °C is attributed to the thermal decomposition of Cu(II)-β-cyclodextrin. The

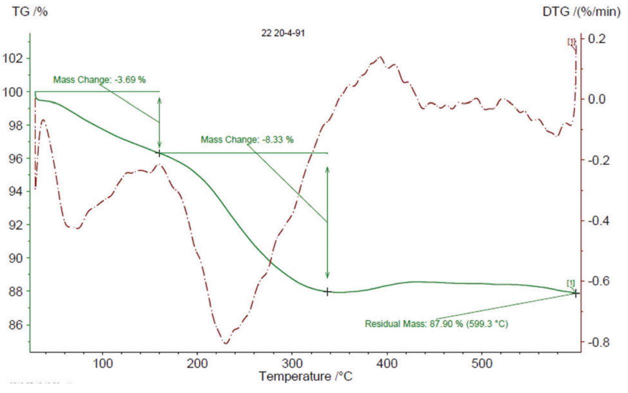


Fig. 2 TGA curve of the Fe_3O_4-supported Cu(II)-β-cyclodextrin.

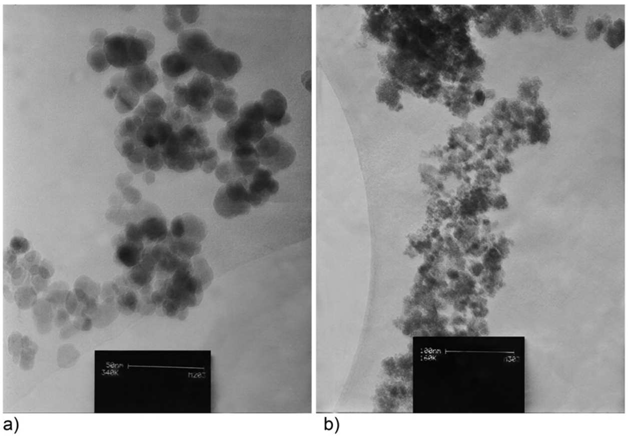


Fig. 3 TEM of Fe_3O_4 (a) and Fe_3O_4-supported Cu(II)-β-cyclodextrin (b).

amount of copper (5.12%) of Fe_3O_4-β-CD-Cu_2 was determined by atomic absorption analysis. The TGA curve and atomic absorption analysis also confirmed the successful supporting of the Cu(II)-β-cyclodextrin complex onto the magnetic surface.

A transmission electron microscope (TEM) was used to obtain direct information about the structure and morphology of the Fe_3O_4-β-CD-Cu_2 nanoparticles. Fig. 3 shows the TEM images of the Fe_3O_4 and Fe_3O_4-β-CD-Cu_2 nanoparticles. The mean diameter of Fe_3O_4 is about 10–20 nm with a mostly spherical shape. The boundary between the particles (low contrast) was not detectable in the TEM of the Fe_3O_4-β-CD-Cu_2 which may be due to interactions between the neighboring particles. No significant layer of Cu(II)-β-cyclodextrin could be observed on these nanoparticles.

The excellent magnetically controllable aggregation behavior of Fe_3O_4-β-CD-Cu_2 was verified by placing a magnet near the vessels containing the aqueous dispersion of the nanoparticles, which were further investigated by vibrating sample magnetometer (VSM) studies. Fig. 4 shows the magnetic hysteresis loops of Fe_3O_4 (a) and Fe_3O_4-β-CD-Cu_2 (b) in an applied magnetic field of 10 000 Oe at 298 K. The hysteresis loops of the Fe_3O_4-β-CD-Cu_2 nanoparticles show a superparamagnetic behaviour with their re-dispersion stability in solution, without aggregation. The saturation magnetization of the Fe_3O_4-β-CD-Cu_2 nanoparticles in Fig. 4b is about 33.0 emu g^{-1}, relatively lower than the unsupported Fe_3O_4 in Fig. 4a, which is due to the non-magnetic properties of the Cu(II)-β-cyclodextrin moiety in the prepared catalyst.

The crystal structures of the Fe_3O_4 and Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles were also studied by XRD analysis (Fig. 5).

The XRD patterns of the Fe_3O_4 and Fe_3O_4-β-CD-Cu_2 nanoparticles indicate six characteristic peaks at 2θ = 30.2°, 35.6°, 43.2°, 53.7°, 57.2°, and 62.9°, as shown in Fig. 5a and b. All diffraction peaks and positions for Fe_3O_4 match well with those from the JCPDS card (no. 76-1849) for the spinel cubic structure of Fe_3O_4. This shows that the prepared Fe_3O_4 nanoparticles are pure with a spinel structure and the supporting of the surface of Fe_3O_4 with Cu(II)-β-cyclodextrin did not result in a phase change of the magnetic nanoparticles. The crystal sizes of the Fe_3O_4 and Fe_3O_4-β-CD-Cu_2 nanoparticles were

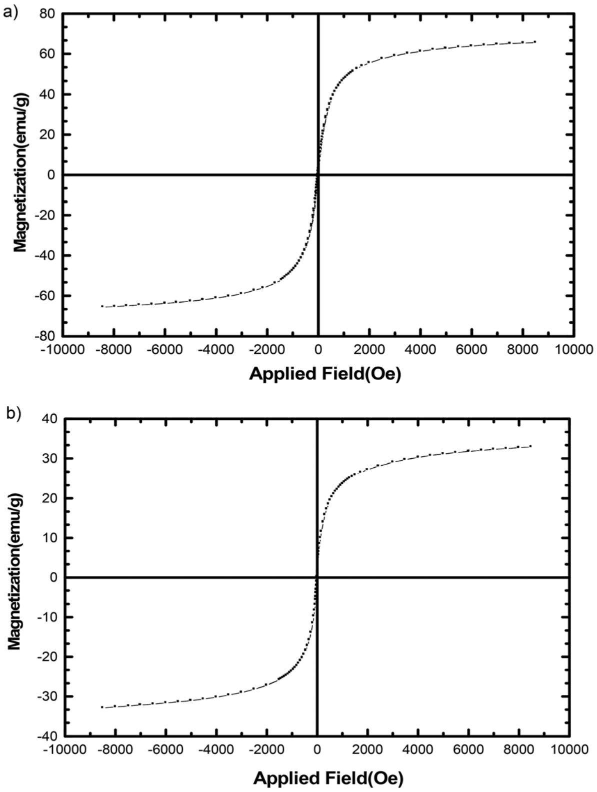


Fig. 4 (a) Magnetic hysteresis loops of the Fe_3O_4. (b) Magnetic hysteresis loops of the Fe_3O_4-supported Cu(II)-β-cyclodextrin.

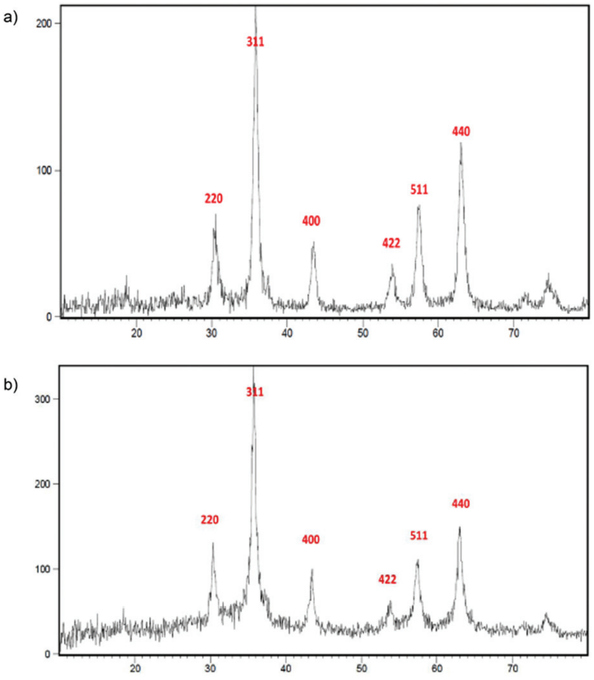


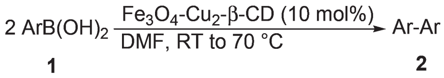
Fig. 5 (a) XRD pattern of the Fe_3O_4. (b) XRD pattern of the Fe_3O_4-supported Cu(II)-β-cyclodextrin.

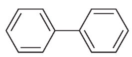
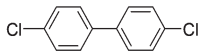
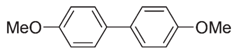
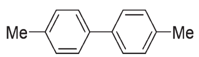
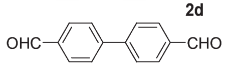
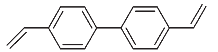
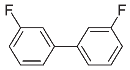
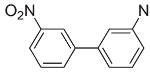
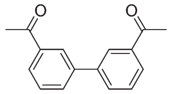
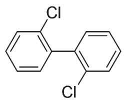
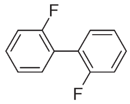
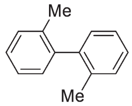
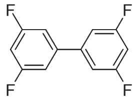
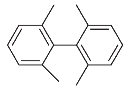
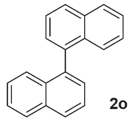
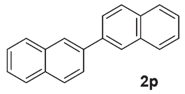
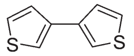
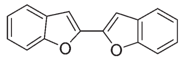
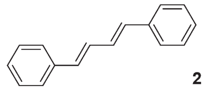
determined from the XRD pattern by using Scherrer's equation.[17] The values provided by the above equation for the Fe_3O_4 and Fe_3O_4-β-CD-Cu_2 nanoparticles were 28 and 17 nm, respectively. This reveals that the Cu(II)-β-cyclodextrin plays a surfactant role, which assists in reducing the nanoparticle size.

The catalytic behavior of the Fe_3O_4-β-CD-Cu_2 nanoparticles was studied for the synthesis of symmetrical biaryls and 1,2,3-triazoles from arylboronic acids. Initially, the homocoupling of phenylboronic acid **1a** was chosen as the model reaction. Recently, we reported on the experimental data for the screening of different copper salts and Cu_2-β-cyclodextrin for the homocoupling of phenylboronic acids.[12a] When the reaction was carried out using Fe_3O_4-β-CD-Cu_2 nanoparticles (0.1 equiv.) with respect to 2 equiv. of **1a** for 3 h at room temperature in DMF, biaryl **2a** was obtained in 90% isolated yield. The blank experiment showed that without the Fe_3O_4-β-CD-Cu_2 nanoparticles, the reaction could not occur. It should be noted that the use of common organic solvents, such as THF or CH_2Cl_2 (as a solvent) did not afford the biphenyl, and low yields (<40%) of biaryl **2a** were obtained using ethanol and methanol as a solvent at room temperature for 24 h. Under the above optimized conditions, the homocoupling of various arylboronic acids was examined using Fe_3O_4-β-CD-Cu_2 nanoparticles in DMF at room temperature in air.

The obtained results are summarized in Table 1. The homocoupling of different *para*-substituted arylboronic acids gave corresponding biaryls in good to excellent yields (Table 1, entries 2–6). An arylboronic acid bearing an aldehyde group, in the *para*-position, gave the corresponding biaryl in 32% yield (Table 1, entry 5). *meta*-Substituted arylboronic acids produced the corresponding products **2g–i** in moderate to good yields (Table 1, entries 7–9). An arylboronic acid bearing a weakly coordinating group of $-NO_2$ could also be used to give the desired product **2h** in a 40% yield (Table 1, entry 8). It is also possible to carry out this homocoupling for *ortho*-substituted arylboronic acids. The homocoupling of different *ortho*-substituted arylboronic acids gave corresponding biaryls in moderate to good yields (Table 1, entries 10–12). Whereas the 3,5-difluorophenylboronic acid provided the corresponding biaryl **2m** in a 75% yield (Table 1, entry 13), while 2,6-dimethylphenylboronic acid failed to give the desired biaryl **2n** due to the steric congestion around the boronic acid (Table 1, entry 14). This result showed that the reaction suffers from substrate size restrictions under these conditions. This method was also applied to the homocoupling of 1- and 2-naphthylboronic acid. 2-Naphthylboronic acid gave the corresponding binaphthyl **2p** in a 90% yield (Table 1, entry15, however, 1-naphthylboronic acid produced the corresponding product **2o** in a lower yield of 50% (Table 1, entry 16), which is possibly due to the steric effect. The homocoupling of thiophen-3-ylboronic acid, as an heteroarylboronic acid, gave a 31% yield of the desired product **2q** (Table 1, entry 17), whereas with benzofuran-2-ylboronic acid gave a 36% yield of the desired product **2r** (Table 1, entry 18). Finally, the reaction of *trans*-2-phenylvinylboronic acid in the presence of

Table 1 Fe_3O_4-β-CD-Cu_2-catalyzed homocoupling reaction of various arylboronic acids



Entry	*T* [°C]	Product **2**	*t* (h)	Yield[a] [%]
1	r.t.	 **2a**	3	90
2	r.t.	 **2b**	2	89
3	r.t.	 **2c**	14	74
4	r.t.	 **2d**	7	66
5	r.t.	 **2e**	10	32
6	r.t.	 **2f**	10	82
7	r.t.	 **2g**	2	85
8	r.t.	 **2h**	4	40
9	r.t.	 **2i**	10	48
10	r.t.	 **2j**	2	80
11	r.t.	 **2k**	1	82
12	r.t.	 **2l**	7	35
13	70	 **2m**	6	75
14	70	 **2n**	24	—
15	r.t.	 **2o**	15	50
16	r.t.	 **2p**	7	90
17	r.t.	 **2q**	2	31
18	r.t.	 **2r**	4	36
19	r.t.	 **2s**	2	50

[a] Isolated yields.

Fe_3O_4-β-CD-Cu_2 nanoparticles gave **2s** in a 50% yield (Table 1, entry 19).

Thus, the conditions reported herein tolerate the homocoupling reaction of a wide variety of arylboronic acids. Of particular note is the homocoupling reaction of the arylboronic acid bearing an aldehyde group in the *para*-position, since the reaction failed in our previous conditions using the Cu(II)-β-cyclodextrin complex as a catalyst.[12a]

On the basis of literature precedents[18] and the structure reported for Cu(II)-β-cyclodextrin,[13] we propose a bimetallic coupling mechanism for Fe_3O_4-β-CD-Cu_2 nanoparticles catalyzed homocoupling reaction of arylboronic acids (Scheme 2).[18] It should be noted that the reaction failed to give a biaryl compound under an atmosphere of argon instead of air.

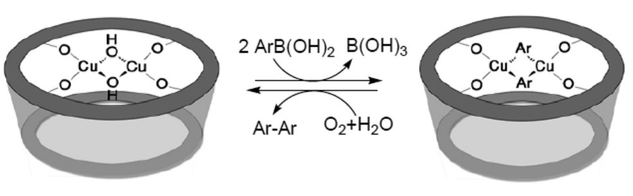
Next we turned our attention to applying this method to the one-pot synthesis of 1,2,3-triazoles *via* the cross-coupling reaction of aryl boronic acids with azides and subsequent click reaction with alkynes (Scheme 3). Recently we reported the experimental data for the screening of several different copper salts and Cu(II)-β-cyclodextrin catalysts in water as a green solvent for the preparation of 1,2,3-triazoles from phenylboronic acids.[12b] According to the previous reported conditions, phenylboronic acid (**1a**) was treated with sodium azide and phenylacetylene in water in the presence of 15 mol% of Fe_3O_4-β-CD-Cu_2 for 4 h at room temperature. As expected, under the reaction conditions the cross coupling reaction and click reaction occurred in one-pot to give **3a** in 95% isolated yield. The blank experiment showed that without the catalyst, the reaction could not occur. Due to these results, the one-pot synthesis of 1,2,3-triazoles from arylboronic acids and alkynes was examined using Fe_3O_4-β-CD-Cu_2 at room temperature in air without any additives.

The results obtained are summarized in Table 2. The one-pot reaction of different substituted arylboronic acids with sodium azide in water followed by a click cyclization reaction with phenylacetylene using Fe_3O_4-β-CD-Cu_2 nanoparticles at room temperature in air, gave the corresponding 1,2,3-triazoles in excellent yields (Table 2, entries 2–10). The arylboronic acid bearing an aldehyde group, in the *para*-position, gave the corresponding triazole product (Table 2, entry 8). It is also possible to carry out this reaction on *ortho*-substituted arylboronic acids (Table 2, entries 2 and 3). This method was also applied to the one-pot synthesis 1,2,3-triazoles of 1- and 2-naphthylboronic acid (Table 2, entries 9 and 10).

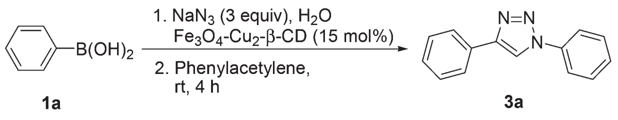
Treatment of phenylboronic acid with sodium azide in water followed by a click cyclization reaction with different substituted phenylacetylenes using Fe_3O_4-β-CD-Cu_2 nanoparticles at room temperature in air, gave desired products in excellent yields (Table 2, entries 11–13). Finally, the reaction of phenylboronic acid with sodium azide in water in the presence of Fe_3O_4-β-CD-Cu_2 nanoparticles followed by a click cyclization reaction with aliphatic alkynes gave the corresponding 1,2,3-triazole in excellent yields (Table 2, entries 14 and 15). Thus, a wide variety of 1,2,3-triazole were synthesized using the conditions reported herein.

The results suggest that the reaction was initiated by the transmetalation of the aryl group from boron to copper *via* the attack of the hydroxide ligand to the oxophilic boron center. The resulting aryl copper intermediate (similar to that in Scheme 2) undergoes subsequent reductive azidation to the aryl azide compound. The 1,2,3-triazole formation proceeds through the formation of copper acetylide followed by coordination of the aryl azide to the copper center of the acetylide initiates an azide–alkyne 1,3-dipolar cycloaddition.[19]

The reusability of the Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles was also studied for both transformations. The Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles were collected by a magnet and washed four times with deionized water and methanol and reused for the homocoupling and one-pot preparation of 1,2,3-triazoles from arylboronic acids (Fig. 6). The catalytic activity did not decrease considerably after four catalytic cycles (Table 3). Atomic absorption analysis of the liquid phase after separation of the catalyst by an external magnet showed that there was no leaching of the copper ions from the catalyst to the reaction mixture.



Scheme 2 The suggested mechanism for the Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticle-catalyzed homocoupling of aryl boronic acids.

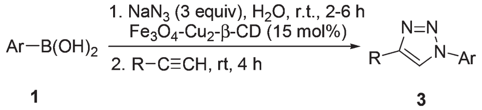


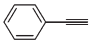
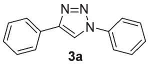
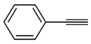
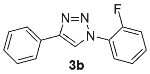
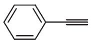
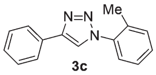
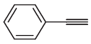
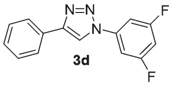
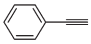
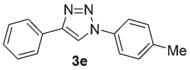
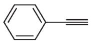
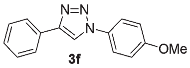
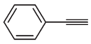
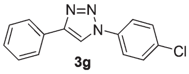
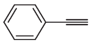
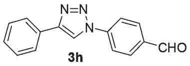
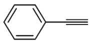
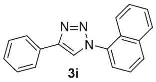
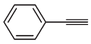
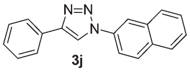
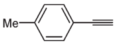
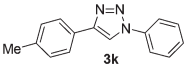
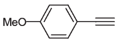
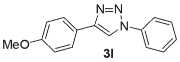
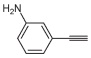
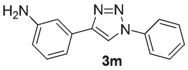
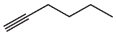
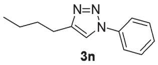
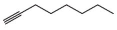
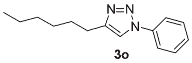
Scheme 3 One-pot synthesis of **3a** using Fe_3O_4-supported Cu(II)-β-cyclodextrin.

Conclusion

In conclusion, we have developed an efficient copper-catalyzed protocol for the preparation of biaryls and 1,2,3-triazoles form arylboronic acids. An efficient, easily recoverable and reusable Fe_3O_4-β-CD-Cu_2 catalyst was prepared and characterized by TEM, XRD, VSM, TGA, and FT-IR spectrometer. The catalyst was suitable for the homocoupling of arylboronic acids for the synthesis of symmetrical biaryls and one-pot synthesis of 1,2,3-triazoles through *in situ* azidation of arylboronic acids and subsequent click cyclization in water. The Fe_3O_4-β-CD-Cu_2 nanoparticles were collected easily by a magnet and the reusability of the prepared nanocatalyst was successfully examined for four runs with only a very slight loss of catalytic activity. This new, efficient process offers several advantages over many of the previously published procedures.

Table 2 Fe_3O_4-supported Cu(II)-β-cyclodextrin-catalyzed one-pot synthesis of 1,2,3-triazoles from arylboronic acids



Entry	Ar (**1**)	Alkyne	Product **3**	*t* (h)	Yield[a] [%]
1	C_6H_5-		 **3a**	4	95
2	*o*-FC_6H_4-		 **3b**	2	95
3	*o*-MeC_6H_4-		 **3c**	2	95
4	3,5-$F_2C_6H_3-$		 **3d**	2	95
5	*p*-MeC_6H_4-		 **3e**	2	95
6	*p*-$MeOC_6H_4-$		 **3f**	3	95
7	*p*-ClC_6H_4-		 **3g**	5	91
8	*p*-$OHCC_6H_4-$		 **3h**	4	93
9	α-Naphthyl		 **3i**	4	90
10	β-Naphthyl		 **3j**	6	96
11	C_6H_5-		 **3k**	3	94
12	C_6H_5-		 **3l**	2	96
13	C_6H_5-		 **3m**	6	60
14	C_6H_5-		 **3n**	6	90
15	C_6H_5-		 **3o**	6	93

[a] Isolated yields.

Experimental

General methods

All melting points were taken on Yanagimoto and Buchi 510 apparatus and are uncorrected. Mass spectra were recorded on a VG Auto Spec. using electron impact ionization (EI) techniques. NMR spectra were obtained on a Bruker Avance 400 NMR Spectrometer (^1H NMR: 400 MHz; ^{13}C NMR: 100 MHz). Gas chromatography was performed on a Varian CP 3800 chromatograph. Analytical TLC was carried out with Merck plates precoated with silica gel 60 F_{254} (0.25 mm thick). Column chromatography was performed either with FLUKA silica gel 60 (70–230 mesh) in common glass columns. Copper sulfate was recrystallized before use. DMF was dried over CaH_2 for 2 h and filtered. Aryl boronic acids and amines were used as received. All solvents were distilled before use.

Fig. 6 Separation of catalyst using an external magnet.

Table 3 Recyclability test of Fe_3O_4-supported Cu(II)-β-cyclodextrin catalyst in the homocoupling (biphenyl, **2a**) and one-pot synthesis of 1,4-diphenyl-*H*-1,2,3-triazole (**3a**) from phenylboronic acids

Product	Yield (%) 1st run	2nd run	3rd run	4th run	Average yield (%)
2a	90	89	87	83	87
3a	95	92	90	87	91

Preparation of Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles

The Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles were prepared by a traditional chemical co-precipitation method.[5d] Cu(II)-β-cyclodextrin (1.5 g, prepared by our previously reported method),[12] $FeCl_3\cdot6H_2O$ (2.36 g), and $FeCl_2\cdot4H_2O$ (0.86 g) were dissolved in distilled water (10 mL) under intense stirring at 90 °C under N_2. Subsequently, ammonia (25%) was added dropwise to the reaction mixture with stirring. The formed nanoparticles were collected with a permanent magnet under the reaction flask and the liquid reaction mixture was removed. The particles were washed with distilled water repeatedly and dried for 24 h at room temperature in a vacuum oven (unsupported Fe_3O_4 nanoparticles were obtained according to the above procedure without adding Cu(II)-β-cyclodextrin).

General procedure for the homocoupling of aryl boronic acids

To a mixture of Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles (0.01 mmol based on copper) in 1 mL DMF was added arylboronic acid (0.2 mmol), and the resulting mixture was stirred at 25–70 °C for 2–24 h. The nanoparticles were collected with a permanent magnet from the reaction mixture. Water (20 mL) was added to the reaction mixture, extracted with CH_2Cl_2 (2 × 20 mL) and dried over Na_2SO_4. The product was purified by immediate flash chromatography (silica gel 60, particle size 230–400 mesh, *n*-hexane–EtOAc) to afford biaryls **2a–s** in 31–90% yields. All products are known and most of them are commercially available (see ESI†).

Gram-scale procedure for the homocoupling of phenyl boronic acid

To a mixture of Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles (0.510 g, 0.41 mmol based on copper) in 5 mL DMF was added phenylboronic acid (1.0 g, 8.2 mmol), and the resulting mixture was stirred at 25 °C for 4 h. The nanoparticles were collected with a permanent magnet from the reaction mixture. Water (100 mL) was added to the reaction mixture, extracted with CH_2Cl_2 (2 × 80 mL) and dried over Na_2SO_4. The product was purified by immediate flash chromatography (silica gel 60, particle size 230–400 mesh, *n*-hexane–EtOAc) to afford 0.57 g of biphenyl **2a** as a white solid.

General procedure for the one-pot synthesis of 1,2,3-triazoles from aryl boronic acids

To a mixture of Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles (0.15 mmol based on copper) in 3 mL distilled water was added arylboronic acid (1 mmol) and sodium azide (3 mmol), and the resulting mixture was stirred at an ambient temperature for 2–6 h. The alkyne (1 mmol) was added to the reaction mixture and the mixture was stirred at an ambient temperature for 4 h. The nanoparticles were collected with a permanent magnet from the reaction mixture and washed with distilled water and methanol repeatedly. Water (50 mL) was added to the reaction mixture and extracted with EtOAc (2 × 20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to give the crude product. The solid was recrystallized from a solvent mixture CH_2Cl_2–*n*-hexane or CH_2Cl_2–methanol to afford purified 1,2,3-triazole **3a–o** in 60–96% yields. All products are known and most of them are commercially available (see ESI†).

Gram-scale procedure for the one-pot synthesis of 1,4-diphenyl-1*H*-1,2,3-triazole (3a) from phenylboronic acids

To a mixture of Fe_3O_4-supported Cu(II)-β-cyclodextrin nanoparticles (1.53 g, 1.23 mmol based on copper) in 15 mL distilled water was added phenylboronic acid (1.0 g, 8.2 mmol) and sodium azide (1.6 g, 24.6 mmol), and the resulting mixture was stirred at ambient temperature for 4 h. Phenylacetylene (0.84 g, 8.2 mmol) was added to the reaction mixture and the mixture was stirred at ambient temperature for 4 h. The nanoparticles were collected with a permanent magnet from the reaction mixture and washed with distilled water and methanol repeatedly. Water (100 mL) was added to the reaction mixture and extracted with EtOAc (3 × 100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 1.59 g of **3a** (88% yield in this scale) as a white solid. The solid was recrystallized from a solvent mixture of CH_2Cl_2–*n*-hexane.

Acknowledgements

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