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PII: S0040-4039(14)02135-2
DOI: http://dx.doi.org/10.1016/j.tetlet.2014.12.069
Reference: TETL 45593

To appear in: *Tetrahedron Letters*

Received Date: 18 August 2014
Revised Date: 10 December 2014
Accepted Date: 12 December 2014

Please cite this article as: Shelkar, R.S., Balsane, K.E., Nagarkar, J.M., Magnetically separable nano CeO_2: A highly efficient catalyst for ligand free direct C–H arylation of heterocycles, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/10.1016/j.tetlet.2014.12.069

Graphical Abstract

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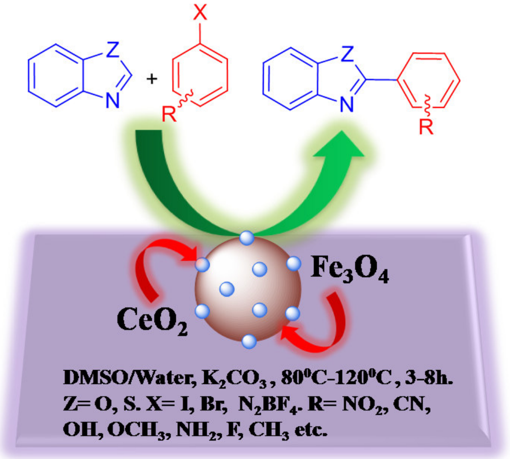

Tetrahedron Letters
journal homepage: www.elsevier.com

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
C-H arylation
Heterocycles
Arenediazonium Salts
Nano CeO_2-Fe_3O_4
Heterogeneous Catalyst

ABSTRACT

An efficient, ligand free, nano CeO_2-Fe_3O_4 catalyzed direct C-H arylation of heteroarenes such as benzoxazole and benzothiazole has been carried out with aryl halides in DMSO or arenediazonium salts in Water. The catalyst exhibited high activity with moderate to excellent product yields under mild reaction conditions. Nano CeO_2-Fe_3O_4 was synthesized and characterized by SEM, TEM, EDAX, XRD, FTIR, DSC-TGA and ICP-MS analysis. The catalytic activity and stability of the catalyst was excellent, even after fifth cycles of recyclability.

1. Introduction

Heterocycles are the key intermediates in synthesis of various pharmaceutical and biologically active products.[1] Therefore, due to the importance and their great applications in medicinal chemistry, the synthesis of these structural motifs is more valuable.[2] The various methods have been developed to synthesize these heterocycles.[3] Among these developed methods, the transition metal catalyzed C-H bond functionalization reaction of arenes and heteroarenes have gained more attention.[4] One of the conventional method for the synthesis of these heterocycles involves the palladium catalyzed cross coupling reactions of either heteroaryl halides with aryl metals or heteroaryl metals with aryl halides.[5] As compared to above methods, the direct C-H functionalization reactions of arenes and heteroarenes provide both ecological and economical benefits. This direct functionalization method is more efficient, as it avoids the pre-functionalization step and the use of stoichiometric amounts of organometallic reagents which pose problems with respective to their synthesis and stability. The reported methods for the synthesis of these heterocycles via direct C-H functionalization of arenes and heteroarenes suffer from certain limitations, which include use of expensive catalyst, high amount of catalyst loading, use of strong base, use of organic ligands and drastic reaction conditions.[6] These issues need to be tackled from 'green chemistry' point of view. Importantly, the recyclability of catalyst is also of great concern for industrial applications which limits the use of homogeneous catalyst. Thus, the development of more efficient, environmentally and economically feasible heterogeneous catalytic system is highly desired to overcome the drawbacks of earlier reported methods.

The first report has been demonstrated by Zhang and co-workers using CuO nanospindles as a catalyst for direct C-H arylation reaction between benzoxazole and iodobenzene under the heterogeneous conditions.[7] Herein we report for the first time, a very simple, economical and environmentally compatible method for the direct C-H arylation of benzoxazole and benzothiazole using nano CeO_2-Fe_3O_4 as a catalyst. Nano CeO_2-Fe_3O_4 catalyst is superior to the reported CuO nanospindle catalyst regarding reaction temperature, reaction time, catalyst concentration, recyclability, requirement of inert atmosphere and prominently substrate study. The magnetic nanoparticles as a catalyst support have been attracting more attention because of high surface area and easy recovery of the catalyst from reaction mass simply by external magnet. This magnetic support proved to be a better choice over the non magnetic materials[7] as it eliminates the tedious workup, centrifugation, filtration and thereby loss in the amount of catalyst. Fe_3O_4 is an ideal material to synthesize the various magnetic nanoparticles supported catalysts.[8] In catalysis, ceria (CeO_2) has gained wide scope due to its efficiency and stability. The magnetic nanoparticles supported ceria have been used for various organic transformations such as oxidation,[9] degradation[10] and in synthesis of carbonyl compounds.[11] In addition to this, ceria has been effectively used as catalyst in various coupling reactions.[12] In continuation, we report the direct C-H arylation reactions using magnetic supported CeO_2 nanoparticles. To the best of our knowledge, use of magnetically separable nano CeO_2-Fe_3O_4 catalyst for direct C-H arylation reaction is not yet reported. The nano CeO_2-Fe_3O_4

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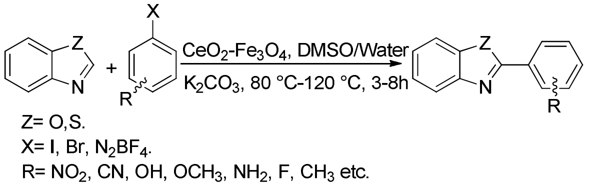
catalyst was synthesized by simple impregnation method.[13] The obtained catalyst was characterized by SEM, TEM, EDAX, XRD, FT-IR, DSC-TGA and ICP-MS analysis.

The activity and stability of synthesized nano CeO_2-Fe_3O_4 catalyst was examined by applying it for direct C-H arylation of benzoxazole or benzothiazole with aryl halides to obtain 2-aryl substituted benzoxazoles or 2-aryl substituted benzothiazoles (Fig. 1). The direct arylation reaction can also be achieved by replacing aryl halides with easily available low cost arenediazonium salts in aqueous medium, using nano CeO_2-Fe_3O_4 as a catalyst. The catalyst showed excellent catalytic activity for C-H arylation reaction due to the high surface area and greater stability.



Z= O,S.
X= I, Br, N_2BF_4.
R= NO_2, CN, OH, OCH_3, NH_2, F, CH_3 etc.

Figure 1. Nano CeO_2-Fe_3O_4 catalyzed direct C-H arylation of heteroarenes with arenes.

2. Characterization of nano CeO_2-Fe_3O_4 catalyst

The obtained nano CeO_2-Fe_3O_4 catalyst was subjected to SEM and TEM analysis to examine the particle size and morphology of nanoparticles Fig.2. Fig. 2b shows that the particles are spherical in shape with size ranging from 3-25nm. The particle size of CeO_2-Fe_3O_4 obtained from TEM analysis matches with that calculated from XRD results using Scherrer equation. The EDAX image exhibits elemental peaks of Ce, Fe and O which confirms presence of nanoparticles of Fe_3O_4 and CeO_2 (Fig. 3).

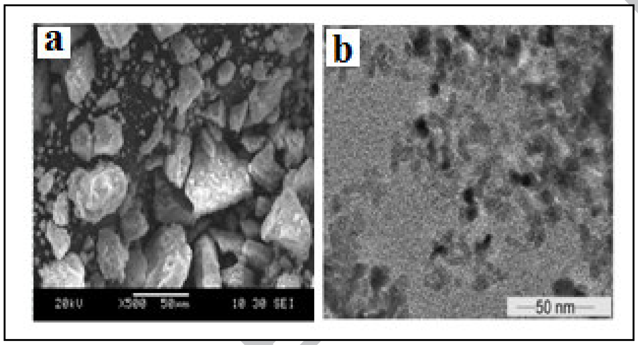


Figure 2. (a) SEM image of CeO_2-Fe_3O_4. (b) TEM image of fresh catalyst.

The XRD pattern of Fe_3O_4 and CeO_2-Fe_3O_4 nanoparticles were shown in Fig. S1. It could be seen that the strong characteristic defraction peaks at 2θ of 33.1° (220), 35.6° (311), 40.8° (400), 54.0° (422), 57.5° (511), 62.4° (440), 71.9° (620) correspond to Fe_3O_4. These peaks resemble that of Fe_3O_4 in cubic phase. The peaks at 2θ of 28.5° (111), 30.0° (200), 43.2° (220), 55.8° (311), and 56.8° (222) correspond to the reflection of Ce. This XRD pattern revealed that the nanocatalyst is composed of Fe_3O_4 and CeO_2. In order to find out surface modifications, FT-IR analysis was carried out in the range of 400 to 4000 cm^{-1}. Fig. S2 shows the FT-IR spectrum of synthesized Fe_3O_4 and CeO_2-Fe_3O_4. The spectra show presence of characteristic peaks for Fe_3O_4 at 3380-3151, 1621, 1402, 632 cm^{-1} and for CeO_2-Fe_3O_4 at 3367, 1647, 1498, 644 cm^{-1}. The peaks in the range of 3380-3151 cm^{-1} are due to the stretching vibration of –OH group. The absorption peaks at 1621 cm^{-1} and 1647 cm^{-1} correspond to the bending vibration of H_2O.[14] The band appeared between 500-700 cm^{-1} corresponds to metal-oxygen (Fe-O) bond which confirmed the presence of Fe_3O_4. The slight shift in absorption peaks clearly indicates successful immobilization of CeO_2 on surface of ferrite. The ICP-MS analysis showed the net Ce content equal to 7.44%.

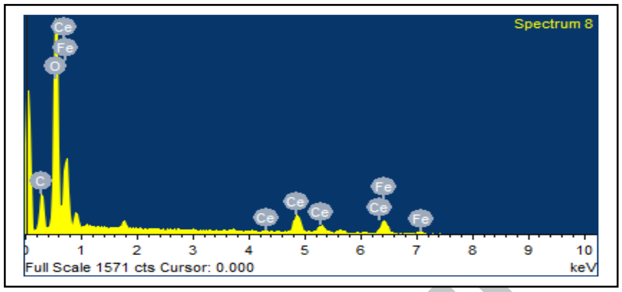
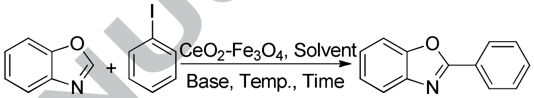


Figure 3. EDAX image of CeO_2-Fe_3O_4.

3. Nano CeO_2-Fe_3O_4 catalyzed direct C-H arylation of benzoxazole

In order to evaluate the catalytic activity of nano CeO_2-Fe_3O_4 catalyst, our initial studies have been focused on the optimization of reaction parameters. The direct C-H arylation of benzoxazole with iodobenzene was chosen as the model reaction (Scheme 1).



Scheme 1. Direct C-H arylation of benzoxazole with iodobenzene.

The influence of solvents has been explored for the model reaction and it was found that amongst the DMSO, DMF, NMP, 1, 4-dioxane and toluene, DMSO was the best suitable solvent which gave excellent yield of coupling product (Table1, entries 1-5). Screening of the various bases such as K_2CO_3, K_3PO_4, NEt_3 and NaOH was also carried out and higher yield was observed with K_2CO_3 base (Table 1, entries 1, 6-8). Furthermore, we examined the effect of temperature on model reaction and 100 °C was found to be the optimum temperature for maximum conversion (Table 1, entries 1, 9-11). The progress of the reaction was monitored by GC analysis. Fig. 4 depicts the progress of reaction with respect to time. It was observed that, the maximum yield of product for model reaction was obtained in 4 hours. Considering the importance of catalyst loading, we employed various amounts of catalyst, ranging from 1 mol% to 7 mol% for model arylation reaction (Table 1, entries 1, 12-14). The yield of arylated product was increased on increasing the catalyst loading from 1 mol% to 5 mol%. Further increase in catalyst loading to 7 mol% showed only 2% increase in the yield. Hence 5 mol% was found as the optimum concentration of the catalyst.

Table 1. Optimization of reaction conditions for direct C-H arylation of benzoxazole with iodobenzene[a].

Entry	Solvent	Base	Catalyst loading	Temperature	Time (h)	Yield (%)[b]
1.	DMSO	K_2CO_3	5 mol%	100°C	4	96
2.	DMF	K_2CO_3	5 mol%	100°C	4	92
3.	NMP	K_2CO_3	5 mol%	100°C	4	83
4.	Dioxane	K_2CO_3	5 mol%	100°C	4	62
5.	Toluene	K_2CO_3	5 mol%	100°C	4	33
6.	DMSO	K_3PO_4	5 mol%	100°C	4	78
7.	DMSO	NEt_3	5 mol%	100°C	4	45
8.	DMSO	NaOH	5 mol%	100°C	4	31
9.	DMSO	K_2CO_3	5 mol%	RT	24	00
10.	DMSO	K_2CO_3	5 mol%	60°C	4	21
11.	DMSO	K_2CO_3	5 mol%	80°C	4	67

12.	DMSO	K_2CO_3	1 mol%	100°C	4	54
13.	DMSO	K_2CO_3	3 mol%	100°C	4	72
14.	DMSO	K_2CO_3	7 mol%	100°C	4	98

[a]Reaction conditions: Benzoxazole (1mmol), Iodobenzene (1mmol), Base (2mmol), Solvent (1mL). [b]GC yield.

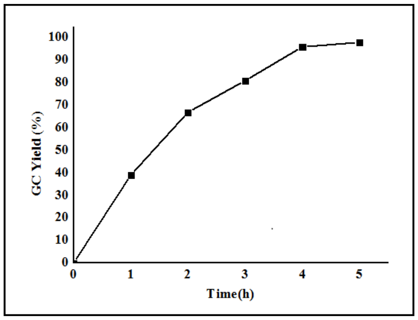
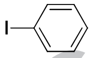
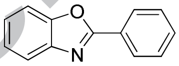
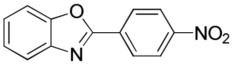
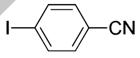
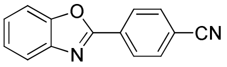
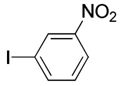
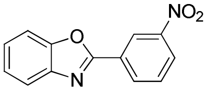
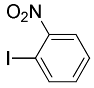
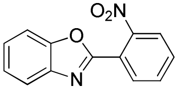
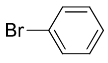
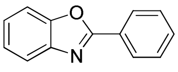
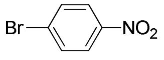
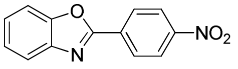
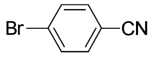
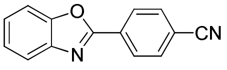
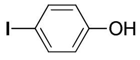
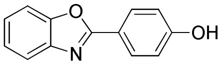
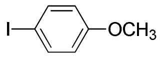
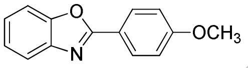
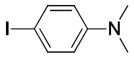
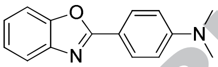
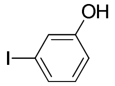
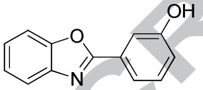
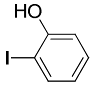
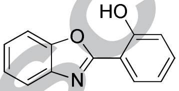
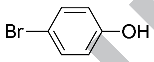
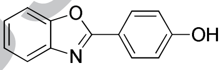
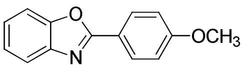
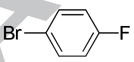
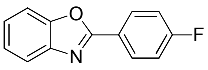
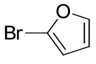
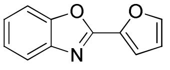


Figure 4. Plot of GC yield versus time for Scheme 1.

The electronic effects of various substituted arenes on arylated product yields have also been studied for this reaction under the established optimal reaction conditions. The arylation reaction has been carried out with substituted iodobenzenes as well as substituted bromobenzenes. This reaction was significantly influenced by electronic nature and position of substituted electron-withdrawing or electron-donating groups on aromatic ring of aryl halides. It was found that iodobenzene derivatives undergo arylation reaction more efficiently with high product yield than the bromobenzene derivatives. The aryl halides containing electron-withdrawing substituents such as 4-nitroiodobenzene, 4-cynoiodobenzene, 3-nitroiodobenzene, 2-nitroiodobenzene, 4-nitrobromobenzene, 4-cynobromobenzene gave excellent yield of desired products (Table 2, entries 1-8). Electron-donating substituents containing aryl halides such as 4-hydroxyiodobenzene, 4-methoxyiodobenzene, 4-aminoiodobenzene, 4-hydroxybromobenzene, 4-methoxybromobenzene, 4-fluorobromobenzene, 3-hydroxyiodobenzene and 2-hydroxyiodobenzene also afforded good to moderate yields (Table 2, entries 9-16). Heterocyclic aryl halide 3-bromofuran was less reactive and yielded 56% product and that too with longer reaction time (Table 2, entry 17).

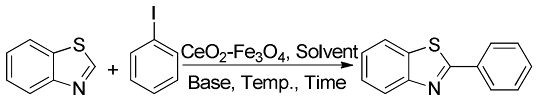
Table 2 Direct C-H arylation reaction of benzoxazole with various aryl halides[a].

Entry	Aryl halides	Products	Time (h)	Yield (%)[b]
1.			4	96(91)[c]
2.			4	98(94)[c]
3.			4	97(92)[c]
4.			4	93(88)[c]
5.			4	87
6.			4	89(83)[c]
7.			4	93(89)[c]
8.			4	91(85)[c]
9.			4	92(87)[c]
10.			4	90(84)[c]
11.			4	85(80)[c]
12.			4	82(77)[c]
13.			4	76
14.			5	84
15.			5	85(76)[c]
16.			5	80(72)[c]
17.			8	56

[a]Reaction conditions: Benzoxazole (1 mmol), Aryl halides (1 mmol), K_2CO_3 (2 mmol), Nano CeO_2-Fe_3O_4 (5 mol%), DMSO (1 mL) at 100 °C. [b]GC yield. [c]Isolated yield in parentheses.

4. Nano CeO_2-Fe_3O_4 catalyzed direct C-H arylation of benzothiazole

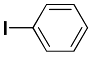
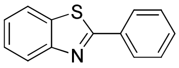
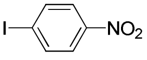
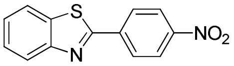
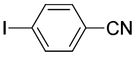
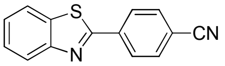
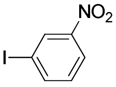
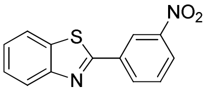
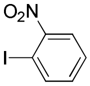
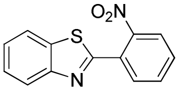
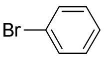
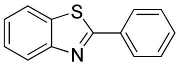
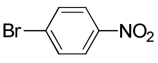
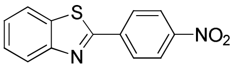
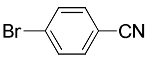
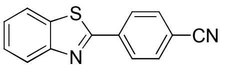
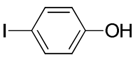
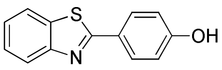
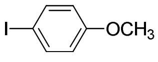
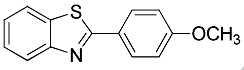
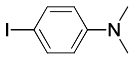
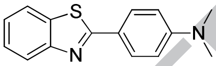
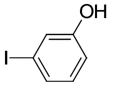
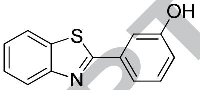
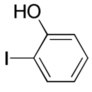
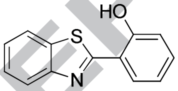
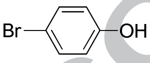
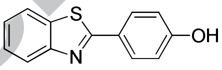
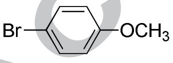
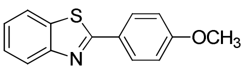
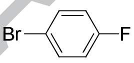
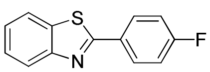
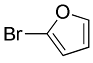
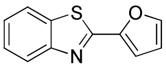
The study was further extended to explore the catalytic activity of nano CeO_2-Fe_3O_4, for arylation reactions of benzothiazole with various aryl halides (Scheme 2).



Scheme 2. Direct C-H arylation of benzothiazole with iodobenzene.

Initially, reaction between benzothiazole and iodobenzene was chosen as model reaction to get the best reaction parameters. The results are summarized in Table S1.The model reaction was monitored by using GC analysis and the progress of the reaction was studied by plotting the graph of GC yield verses time (Fig. 5). The DMSO solvent (1 mL), K_2CO_3 base (2 mmol), 5 mol% catalyst, at 120 °C temperature and 5h reaction time are the optimized reaction parameters which gave maximum product yield for the model reaction. We next screened various substituted aryl halides with benzothiazole under the optimized reaction conditions. The catalyst was more reactive towards aryl halides containing electron-withdrawing substituents, giving excellent product yields as compared to electron-donating ones (Table 3, entries 1-16). Similarly, heterocyclic aryl halide also coupled with benzothiazole giving corresponding product with moderate yields (Table 3, entry 17).

Table 3 Direct C-H arylation reaction of benzothiazole with various aryl halides[a].

Entry	Aryl halides	Products	Time (h)	Yield (%)[b]
1.			5	83(79)[c]
2.			5	89(83)[c]
3.			5	86(82)[c]
4.			5	81(76)[c]
5.			6	75
6.			6	80(74)[c]
7.			5	84(77)[c]
8.			5	78(73)[c]
9.			6	72(68)[c]
10.			6	70(64)[c]
11.			6	67(61)[c]
12.			6	64
13.			6	59
14.			7	63(57)[c]
15.			7	59(52)[c]
16.			6	61(58)[c]
20.			8	41

[a]Reaction conditions: Benzothiazole (1 mmol), aryl halides (1 mmol), K_2CO_3 (2 mmol), Nano CeO_2-Fe_3O_4 (5 mol%), DMSO (1 mL) at 120 °C. [b]GC yield. [c]Isolated yield in parentheses.

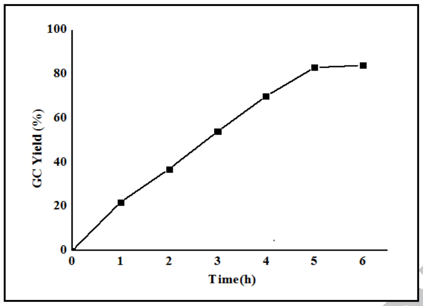
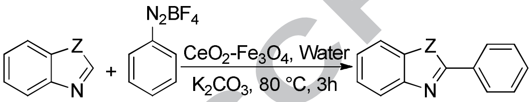


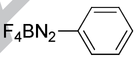
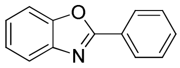
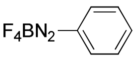
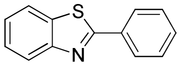
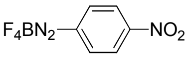
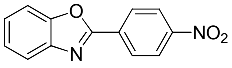
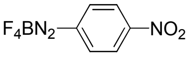
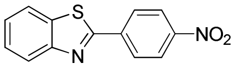
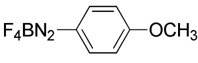
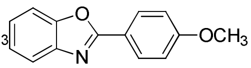
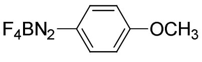
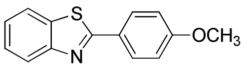
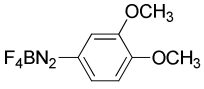
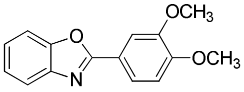
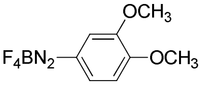
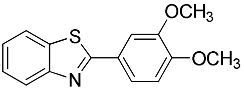
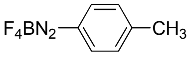
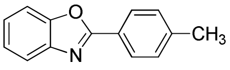
Figure 5. Plot of GC yield versus time for Scheme 2.

5. Nano CeO_2-Fe_3O_4 catalyzed direct C-H arylation of benzoxazole and benzothiazole with arenediazonium salts



Scheme 3. Direct C-H arylation of benzoxazole and benzothiazole with arenediazonium salts.

Table 4. Direct C-H arylation reaction of benzoxazole and benzothiazole with various arenediazonium salts[a].

Entry	Arenediazonium salts	Products	Time (h)	Yield (%)[b]
1.			3	87(83)[c]
2.			3	73(66)[c]
3.			3	92(87)[c]
4.			3	74
5.			3	78(70)[c]
6.			3	65
7.			4	57
8.			5	53(47)[c]
9.			3	64

[a]Reaction conditions: Benzoxazole/Benzothiazole (1 mmol), Arenediazonium salts (1 mmol), K_2CO_3 (2 mmol), Nano CeO_2-Fe_3O_4 (5 mol%), Water (1 mL) at 80 °C. [b]GC yield. [c]Isolated yield in parentheses.

Iodobenzene and bromobenzene derivatives are more expensive. Keeping this in mind, we have employed arenediazonium salts which are easily available and cheaper for arylation of benzoxazole or benzothiazole (Scheme 3). The arylation reaction of benzoxazoles or benzothiazoles with arenediazonium salts in aqueous medium is the greener route which is the merit of nano CeO_2-Fe_3O_4 catalyst. It was observed that coupling reactions between benzoxazoles or benzothiazole with various arenediazonium salts are effectively carried out by using nano CeO_2-Fe_3O_4 (Table 4, entries 1-9).

6. Recyclability of nano CeO_2-Fe_3O_4 in direct C-H arylation reaction of benzoxazole with iodobenzene.

Reusability of nano CeO_2-Fe_3O_4 catalyst was tested as it is one of the important parameters regarding industrial application of heterogeneous catalytic systems. Initially the fresh catalyst was employed to arylation reaction of benzoxazole with iodobenzene under the optimized reaction conditions. After completion of reaction, the catalyst was separated from reaction mass by using external magnet and washed with ethanol followed by drying. The recovered catalyst was reused for next batch of same reaction under similar reaction conditions using fresh starting substrates. This procedure was repeated up to ten cycles. The results obtained from GC analysis clearly indicate that the catalyst has fairly good activity over the ten cycles of the reaction (Fig. 6). To verify the leaching of catalyst, we have carried out arylation reaction between benzoxazole and iodobenzene. The catalyst was separated after 1h from reaction mass by using external magnet. The GC conversion was found to be 39% at this stage. No further progress of the reaction was observed after continuing the reaction for 4h in the absence of the catalyst (Fig. 7). The leaching was also studied by ICP-MS analysis, and no significant leaching of ceria was observed.

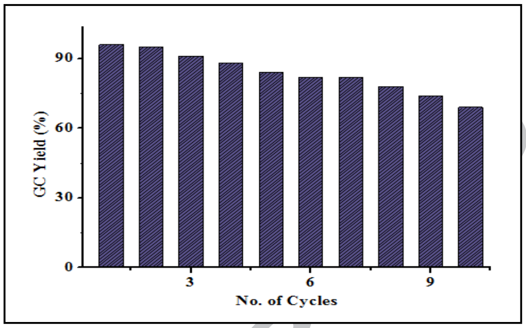


Figure 6. Recyclability of nano CeO_2-Fe_3O_4 in arylation reaction.

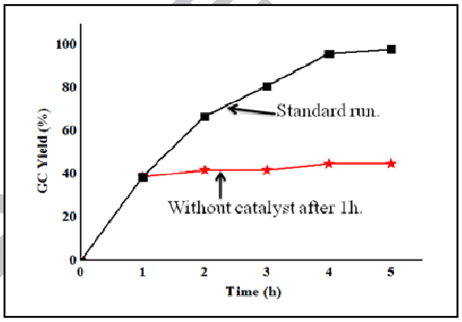


Figure 7. Hot filtration curve.

In conclusion, we are presenting the first report on the magnetically separable, nanosized CeO_2-Fe_3O_4 catalyzed direct C-H arylation reaction of benzoxazole or benzothiazole with various arenes under the ligand free conditions. The catalyst preparation and arylation reaction methodology were very simple, economical and environmentally favourable, giving excellent yields of arylated products. In addition to this, the catalyst showed recyclability up to ten cycles, with marginal loss in the catalytic activity.

Acknowledgments

The authors are very thankful to the UGC-UPE-2756, Green Technology centre, New Delhi, India for awarding the fellowship.

References and notes

1. Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. *Org. Biomol. Chem.* **2006**, *4*, 2337; Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402; Besselievre, F.; Piguel, S.; Mahuteau-Betzer, F.; Grierson, D. S. *Org. Lett.* **2008**, *10*, 4029-4032; Yoshizumi, T.; Tsurugi, H.; Satoh, T.; Miura, M. *Tetrahedron Lett.* **2008**, *49*, 1598-1600; Shelkar, R.; Singh, A.; Nagarkar, J. *Tetrahedron Lett.* **2013**, *54*, 106-109; Ranjit, S.; Liu, X.; *Chem. Eur. J.* **2011**, *17*, 1105-1108.
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Highlights

- Nano CeO_2-Fe_3O_4 was used for direct C-H arylation of heterocycles.
- The system was optimized with respect to various reaction parameters.
- Arylation reaction was also carried out with arenediazonium salts in water.
- The simple methodology gives excellent yield of arylated products.
- The catalyst should be reused up to five cycles.