

Short communication

α -Arylation of oxindoles using recyclable metal oxide ferrite nanoparticles: Comparison between the catalytic activities of nickel, cobalt and copper ferrite nanoparticles



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ABSTRACT

Three different spinel metal oxide catalytic systems including NiFe_2O_4 , CuFe_2O_4 and CoFe_2O_4 were synthesized using co-precipitation technique and their catalytic activities were compared to each other in α -arylation of oxindole derivatives under the optimized reaction conditions. Both nickel ferrite and copper ferrite magnetic nanoparticles show approximately the same behavior in these reactions but cobalt ferrite ones indicate slightly different properties and were not as good as the other two catalysts. These superparamagnetic catalysts allowed that α -arylation of different types of oxindoles will occur in high yields under mild conditions and at very short times.

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1. Introduction

One of the important structures that can be found most frequently in many natural products, pharmaceutical targets and biologically active molecules is oxindole and its derivatives [1,2]. These compounds exhibit antibacterial and antifungal activities [3]. These C-3 functionalized oxindoles can be used as drugs against a variety of neurodegenerative disorders [5] and also show anti-tumor [6] and anti-HIV properties [7]. One of the most important oxindoles are C-3 aryl ones playing a significant role in some biological routes [2,4]. A number of techniques have been reported for synthesizing C-3 functionalized derivatives of oxindoles, especially C-3 arylated ones [4,8–14].

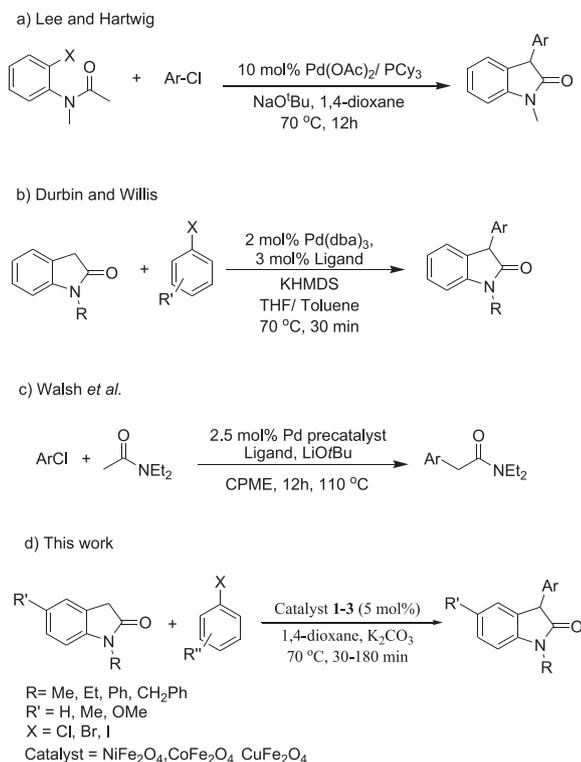
Metal-catalyzed routes for this purpose are of most important and efficient methods. Previously reported methodologies based on classical chemical reactions [4,15–20] do not work when the substrate contained the oxindole core. In such cases, intermolecular arylation of the C-3 position of oxindole in the presence of a metal-based catalyst is what required, something named as metal-catalyzed α -arylation of carbonyl compounds [11–14]. Hartwig et al. in 2001 reported intramolecular α -arylation of oxindoles using Pd^0 as catalyst to give 3,3-disubstituted oxindoles (Scheme 1a) [4]. In 2008, Durbin and Willis synthesized α -arylated oxindoles using $\text{Pd}(\text{dba})_2$ as catalyst (Scheme 1b). Walsh et al. in 2013 reported α -arylation of acetamides with aryl chlorides in the presence of a palladium precatalyst and a phosphinic ligand

(Scheme 1c) [21]. Application of a strong base is necessary in all these reports to deprotonate the amidic α -proton. These works use palladium with phosphine ligands that suffer from some drawbacks. For example, palladium is a high cost, toxic and moisture-sensitive transition metal that often needs to certain types of ligands, especially phosphinic ones, to be active and effective [22]. The catalytic systems employed by Walsh and also by Durbin and Willis are both homogeneous and none of them are recyclable. On the other hand, application of ligands in many organic reactions can be supposed as a source of limitation because many of these ligands are not available easily. These reactions are also performed under approximately harsh reaction conditions. There are some examples of α -arylation of carbonyl compounds using other transition-metal based catalysts, especially cuprous or cupric salts [23]. Application of such catalysts is also accompanied with some drawbacks. Cu(I) salts are also air-sensitive and require harsh conditions to be kept stable. Furthermore, these metal sources may contaminate the final products leading to limitations on their usage as drugs.

On the other hand, among the carbonyl containing compounds, α -arylation of amide enolates is most challenging due to high pK_a values of the substrates [14]. As far as we know, there are a few reports regarding metal-catalyzed C-3 arylation of oxindoles [24]; so, introducing new efficient methodologies to this end could be of high importance. Due to the limitations of previous catalytic systems, there remains a need for introducing low-cost and readily available catalysts with high efficiency. Magnetic metal oxide nanoparticles, especially those with spinel structure, have attracted a lot of attention recently. In fact, the presence of two transition metals in these systems could enhance their catalytic

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Scheme 1. Comparison of previous reports on α -arylation of oxindoles with this work.

activity because of the synergistic effect between the two metals [25,26]. These heterogeneous catalysts not only have considerable catalytic activity, but also can be synthesized easily. In addition, they can be recovered simply from the reaction media using an external magnetic field and can be reused for several times. These are the main advantages of these systems especially from the industrial view point [27–29].

Considering all these facts and many others, we decided to employ superparamagnetic nickel ferrite nanoparticles as catalyst in the α -arylation of oxindoles. These spinel nanoparticles were synthesized and characterized previously by our group and their excellent catalytic activity in various C–C and C–heteroatom coupling reactions was demonstrated [30,31]. Herein, in continuation of our previous works, the applicability of these magnetic nanoparticles as an efficient catalytic system in α -arylation of oxindoles is reported. Different types of oxindole derivatives having substituents on the aromatic ring or without that were synthesized and used as substrate in this reaction. Results show that compared to the previously reported Pd- or Cu-catalyzed α -arylation reactions [14,24,32], this procedure could functionalized C-3 position of oxindoles successfully with very good yields in reasonably shorter reaction times. These remarkable results encouraged us to do a comparative investigation to find a catalyst with best catalytic behavior for this reaction. To this end, two additional metal oxides, i.e. copper ferrite and cobalt ferrite nanoparticles were synthesized [30] and their activity as catalyst was examined in the α -arylation of oxindoles under the same reaction conditions.

2. Results and discussion

Nickel, cobalt and copper ferrite magnetic nanoparticles were synthesized using co-precipitation method [30]. These nanoparticles were used as catalyst in the α -arylation reaction of oxindole derivatives and their activities were compared to each other.

Optimum reaction conditions were determined initially using nickel ferrite nanoparticles as catalyst. The reaction between *N*-methyl oxindole and bromobenzene was selected as the model reaction and the effect of each of the parameters on this reaction was considered

carefully (Table 1). The reaction that resulted in the formation of two products, **1a** and **1b**, depends on the reactant ratios and other conditions.

As can be seen in Table 1, when the reaction is conducted in DMSO, Toluene and NMP, the formation of byproduct **1b** is unavoidable. The model reaction also was performed in H₂O as the green solvent but its yield was not good. Finally, using 1,4-dioxane as solvent, not only yield of the reaction was much better, but also the ratio of products **1a** to **1b** is very high and it can be said that the reaction approximately resulted in the selective formation of **1a** as the sole product (Table 1, entry 4).

The effect of various organic and inorganic bases also was investigated (Table 1, entries 4, 6–9). Both K₂CO₃ and KO^t-Bu resulted in full conversion of the substrate under these reaction conditions; however, using KO^t-Bu as base, higher amount of byproduct, **1b**, is produced in the reaction (Table 1, entry 8). Therefore, K₂CO₃ was selected as the best base (Table 1, entry 4).

In order to optimize the amount of catalyst required for such transformation, the model reaction was repeated in the absence of catalyst and also in the presence of 1, 2, 5 and 10 mol% of NiFe₂O₄ nanoparticles (Table 1, entries 4, 10–13). As it is shown in Table 1, the reaction does not progress in the absence of catalyst. In addition, when 1 or 2 mol% of nickel ferrite nanoparticles were used, reaction rate is not so high and their yields are moderate; however, when the catalyst concentration increases to 5 mol%, very good yield could be obtained in a reasonable time and with minimum formation of the byproduct (Table 1, entry 13). Further increase in the amount of catalyst (up to 10 mol%) does not give rise to higher reaction rate and better yields of **1a**.

Conducting the model reaction at 100 °C, 70 °C, 45 °C and also at room temperature Table 1, entries 13–16 showed that although the reaction rate and conversion is relatively low at 45 °C and room temperature, the results obtained at 70 °C were excellent. At 100 °C, the reaction rate was not increased but higher amount of **1b** was formed.

In the final step, reactant ratio was investigated. Results indicated that decreasing the amount of bromobenzene to 1 equivalent caused the formation of **1a** as the sole product (Table 1, entry 17).

Table 1
Screening the reaction conditions for α -arylation of oxindole derivatives.^a

Entry	Solvent	Base	Catalyst (mol%)	Temperature (°C)	Yield (%) ^b	
					1a	1b
1	DMSO	K ₂ CO ₃	10	100	62	14
2	Toluene	K ₂ CO ₃	10	100	53	11
3	H ₂ O	K ₂ CO ₃	10	100	44	6
4	1,4-Dioxane	K ₂ CO ₃	10	100	86	7
5	NMP	K ₂ CO ₃	10	100	66	13
6	1,4-Dioxane	Cs ₂ CO ₃	10	100	71	8
7	1,4-Dioxane	NaOAc	10	100	45	11
8	1,4-Dioxane	KO ^t Bu	10	100	82	12
9	1,4-Dioxane	Et ₃ N	10	100	64	10
10	1,4-Dioxane	K ₂ CO ₃	None	100	Trace	0
11	1,4-Dioxane	K ₂ CO ₃	1	100	43	Trace
12	1,4-Dioxane	K ₂ CO ₃	2	100	61	3
13	1,4-Dioxane	K ₂ CO ₃	5	100	85	6
14	1,4-Dioxane	K ₂ CO ₃	5	70	86	4
15	1,4-Dioxane	K ₂ CO ₃	5	45	52	0
16	1,4-Dioxane	K ₂ CO ₃	5	RT	43	0
17 ^c	1,4-Dioxane	K ₂ CO ₃	5	70	85	0

^a Reaction conditions: *N*-methyl oxindole (1 mmol), Bromobenzene (1.2 mmol), Base (1.1 mmol), Catalyst, Solvent (2 mL), Temperature (°C).

^b Isolated yield.

^c *N*-methyl oxindole (1 mmol), Bromobenzene (1 mmol).

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