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Superparamagnetic nanoparticles as a recyclable heterogeneous catalyst for the direct synthesis of carbamates containing biothiazole moiety

Nguyen Kim Chung[1], Tran Nhut Kien[1], Dang Huynh Giao[1,2], Le Thanh Dung[1*] and Phan Thanh Son Nam[1]

[1]*Faculty of Chemical Engineering, HCMC University of Technology, VNU-HCM*

[2]*College of Engineering Technology, Can Tho University*

[*]*Correspondence: Le Thanh Dung (email: ltdung@ctu.edu.vn)*

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ABSTRACT

Superparamagnetic copper ferrite nanoparticles were utilized as a recyclable heterogeneous catalyst for the cross-dehydrogenative coupling of N,N-disubstituted formamides with phenols. This routine allowed the creation of a hybrid benzothiazole-carbamate moiety under heterogeneous catalysis. These products possess both carbamate and benzothiazole moieties, thus taking profits from both structures with regard to pharmaceutical and biological activities. Employing a catalytic portion of the superparamagneti cnanoparticles, hybrid benzothiazole-carbamate structures could be produced with reasonable yields within 2 hrs. It was possible to recover the nanoparticles by simple magnetic separation, and reutilize them for the reaction without a significant decline in catalytic efficiency.

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1 INTRODUCTION

Catalysis has been considered as the spirit of the chemical industry, and using heterogeneous catalysts in the production of fine chemicals and pharmaceuticals for straightforward catalyst recycling is a long-established target of catalysis discipline (Cano *et al.*, 2015; Kausik *et al.*, 2016). ‘‘Nanocatalysis’’ has emerged as an swiftly developing field during the last decade (Purbia and Paria, 2015; Stark *et al.*, 2015), and active nanoparticles have been explored as a link between homogeneous and heterogeneous catalysts (Ranganath and Glorious., 2011; Zhang *et al.*, 2014; Peiris *et al.*, 2016). If it is possible to reduce the catalyst particle size to nanometer dimensions, all of the areas on the external surface of the catalyst might be beneficial for the conversion, and hence its activity could be remarkably polished (Duan *et al.*, 2015; Gawande *et al.*, 2015; Sharma *et al.*, 2015). However, the collection and recycling of the nanoparticles is really troublesome, and the problem still continues to be solved (Hu *et al.*, 2014). Superparamagnetic nanoparticles could integrate superiority of high dispersion and high reactivity with easy separation via magnetic isolation protocol (Ranganath and Glorious, 2011). Indeed, catalyst systems based on either functionalized or unfunctionalized superparamagnetic nanoparticles have been employed in organic synthesis. Unfunctionalized superparamagnetic nanoparticles have recently appeared as effective heterogeneous catalysts for the aldehyde-free synthesis of propargylamines (Nguyen *et al.*, 2014), the synthesis of 1,4-dihydropyridines and 2-amino-4-(indol-3-yl)-4*H*-chromenes (Rajesh *et al.*, 2014), the synthesis of 3,4-dihydropyrimidine-2(1*H*)-ones (DHPMs) (Dey *et al.*, 2015), the regioselective hydroboration of alkynes (Mohan and Park, 2016), and the arylation of oxindoles (Moghaddam *et al.*, 2016).

Organic carbamates are a momentous category of pharmaceutically and biologically alluring compounds that customarily come about in many pharmaceuticals, naturally bioactive products, , and agrochemicals (Kathiresan and Velayutham, 2015; Wang *et al.*, 2015). Established synthetic protocols employed hazardous reagents, and should be refined utilizing greener approaches (Saberi *et al.*, 2016). Krogul and Litwinienko (2015) previously demonstrated the synthesis of carbamates by oxidative carbonylation between anilines and CO/O_2 mixture employing $PdCl_2(X_nPy)_2$ complexes as catalyst. Reddy and co-workers proposed a direct conversion of *N*-aryl formamides to carbamates employing hypervalent iodine (Reddy et al., 2016). Recently, Ali *et al.* (2015) revealed the first report of the generation of carbamates from dialkylformamides and phenols carrying benzothiazole directing substituents utilizing copper acetate catalyst. These products possess both carbamate and benzothiazole portions, thus taking benefits from both structures with regard to biological activities. However, the catalyst *could not be recycled and reused*. Herein, the purpose of this study is to present the synthesis of carbamates containing benzothiazole moiety by direct coupling between phenols and *N,N*-disubstituted formamides employing unfunctionalized $CuFe_2O_4$ superparamagnetic nanoparticle as a robust, effective and recyclable catalyst.

2 MATERIALS AND METHODS

The superparamagnetic nanoparticles $CuFe_2O_4$ were supplied by Sigma-Aldrich. The material was subsequently characterized by many analysis protocols. In an illustrative experiment, 2-(2-hydroxyphenyl) benzothiazole (0.1136 g, 0.5 mmol) was dissolved in *N,N'*-diethylformamide (DEF, 1.5 ml, 19 mmol), and the solution was added into an 8 mL vial consisting of the pre-calculated quantity of catalyst. The catalyst amount was determined with respect to the copper/2-(benzo[d]thiazol-2-yl) phenol mole fraction. Subsequently, *tert*-butyl hydroperoxide (*t*BuOOH, 70% wt. in water; 0.291 mL, 2.0 mmol) was added to the vial, and the resulting mixture was magnetically stirred at 100ºC for 60 mins under air. After that, the reactor was cooled down to room temperature, then diphenyl ether (0.0851 g, 0.5 mmol) as an internal standard was introduced to the reaction mixture. Samples were taken, diluted with ethyl acetate (3 mL), stirred forcefully with anhydrous Na_2SO_4 to remove water residue, and analyzed by gas chromatography (GC) regarding diphenyl ether. The *o*-(2-benzothiazolyl) phenyl diethylcarbamate was purified using column chromatography. The product specification was additionally validated by ^{1}H NMR and ^{13}C NMR. To inspect the reusability of $CuFe_2O_4$, the nanoparticles were separated by magnetic decantation, washed carefully with DEF and methanol, dried in a Shlenk line at 150ºC under vacuum in 6 hrs., and reutilized for new catalytic run.

3 RESULTS AND DISCUSSION

3.1 Characterization of catalysis

The superparamagnetic nanoparticles $CuFe_2O_4$ were characterized by utilizing several conventional analysis methods. X-ray powder diffraction result of the nanoparticles showed that no impurity peak was detected (Fig. 1). Scanning electron microscopy (Fig. 2) and transmission electron microscopy (Fig. 3) pictures revealed that the nanoparticles possessed diameters of less than 50 nm. A vibrating sample magnetometer was utilized to investigate magnetic properties of the nanoparticles, with an applied field ranging from -15000 Oe to 15000 Oe being explored. The magnetization curves were noticed to be entirely reversible at room temperature, verifying that the nanoparticles should be superparamagnetic (Fig. 4). The magnetization curves also indicated that the nanoparticles exhibited saturation magnetization value of 30 emu/g.

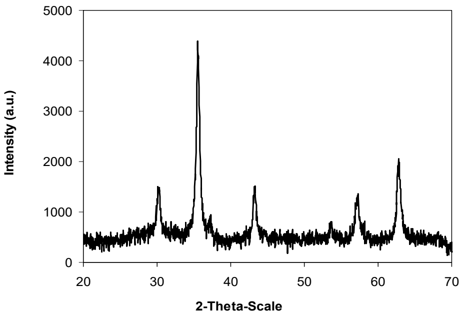

Fig. 1: X-ray powder diffractograms of the $CuFe_2O_4$ nanoparticles

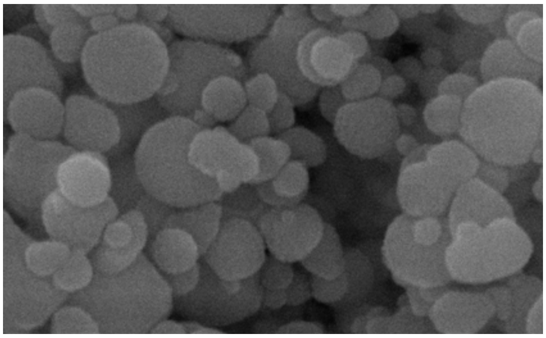

Fig. 2: SEM micrograph of the $CuFe_2O_4$ nano-particles

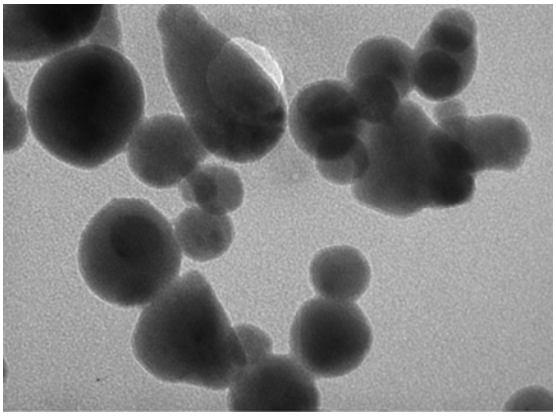

Fig. 3: TEM micrograph of the $CuFe_2O_4$ nanoparticles

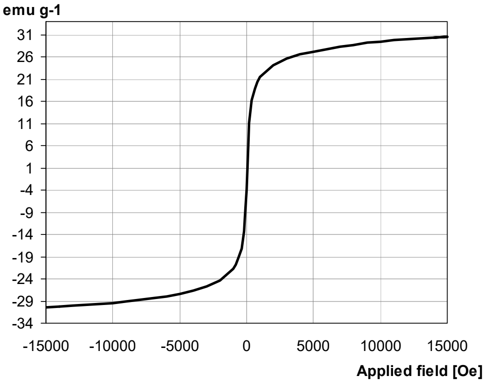

Fig. 4: Magnetization curves for the $CuFe_2O_4$ nanoparticles

3.2 Catalytic studies

The superparamagnetic nanoparticles were evaluated for their activity in the reaction between 2-(2-hydroxyphenyl) benzothiazole and DEF to produce *o*-(2-benzothiazolyl)phenyl diethylcarbamate as the major product (Fig. 5). In this protocol, the benzothiazole acts as a directing substituent, facilitating the cross-dehydrogenative coupling conversion. This routine allowed the creation of a hybrid benzothiazole-carbamate moiety under heterogeneous catalysis. Introductory studies concentrated on the consequence of temperature to the diethylcarbamate yield. The reaction was conducted in the presence of 5 mol% catalyst for 60 mins, employing 4 equivalents of aqueous *t*BuOOH oxidant, with 26 equivalents of DEF, at room temperature, 60ºC, 80ºC, 100ºC, and 120ºC, respectively. It was noted that the reaction could produce the expected product in 65% yield after 60 mins at 100ºC. Implementing the experiment at higher than 100 ºC was realized to be pointless as the yield of *o*-(2-benzothiazolyl) phenyl diethylcarbamate was not expanded anymore. Lowering the reaction temperature caused a deterioration in the yield of the expected product. The $CuFe_2O_4$-catalyzed coupling reaction could not carry on at 60ºC, and only 3% yield was monitored after 60 mins (Fig. 6).

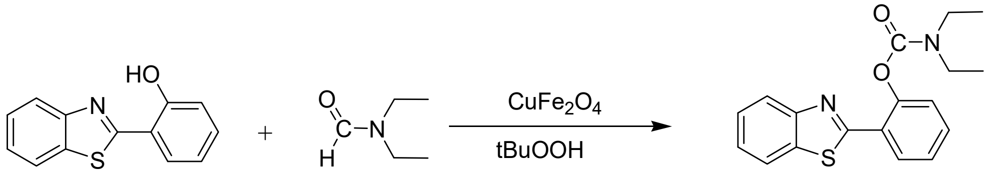

Fig. 5: The formation of hybrid carbamate-benzothiazole skeleton utilizing nano $CuFe_2O_4$ catalyst

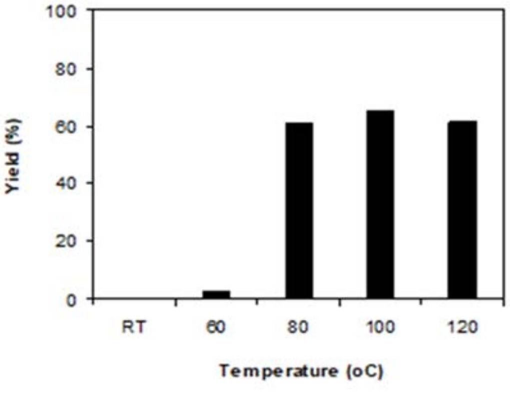

Fig. 6: Effect of temperature on *o*-(2-benzothiazolyl)phenyl diethylcarbamate yield

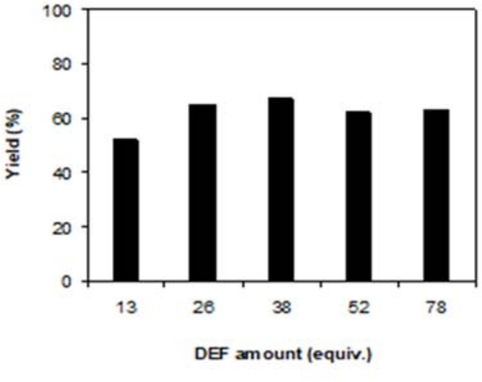

Fig. 7: Impact of DEF amount on *o*-(2-benzothiazolyl)phenyl diethylcarbamate yield

Having these data in mind, the 2-(2-hydroxyphenyl) benzothiazole:formamide mole fraction on the preparation of *o*-(2-benzothiazolyl) phenyl diethylcarbamate was investigated. In this study, DEF, the second reactant, was also the solvent for the conversion using the nano catalyst. Undoubtedly, the rate of liquid phase organic reactions utilizing solid catalysts might be notably manipulated by the quantity of the solvent attributable to the mass transfer phenomenon. In the previous description of the synthesis of carbamates from formamides and phenols possessing benzothiazole directing groups with copper acetate catalyst, generally 26 equivalents of DEF were used for the reaction (Ali *et al.,* 2015). The reaction was conducted at 100ºC in the presence of 5 mol% catalyst for 60 mins, utilizing 4 equivalents of aqueous *t*BuOOH oxidant, with 13, 26, 38, 52, and 78 equivalents of DEF, respectively. As pointed out earlier, the reaction using 26 equivalents of DEF could provide 65% yield after 60 mins. Diminishing the quantity of DEF to 13 equivalents eventuated a momentous reduction in the yield of the expected product. It was possible to improve the yield of *o*-(2-benzothiazolyl) phenyl diethylcarbamate to 67% after 60 mins when 38 equivalents of DEF were employed. Utilizing larger amounts of DEF was not a good option for the conversion, as the reaction yield was decreased (Fig. 7).

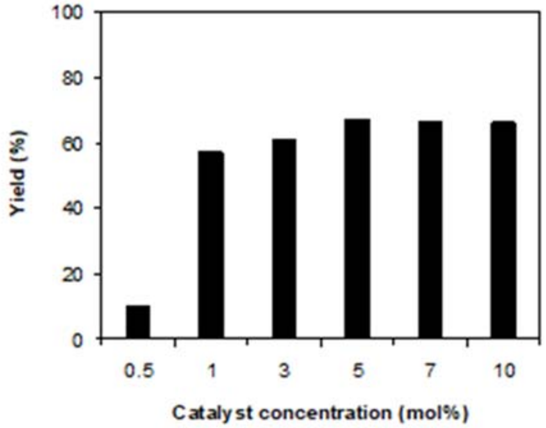

Fig. 8: Influence of catalyst concentration on o-(2-benzothiazolyl)phenyl diethylcarbamate yield

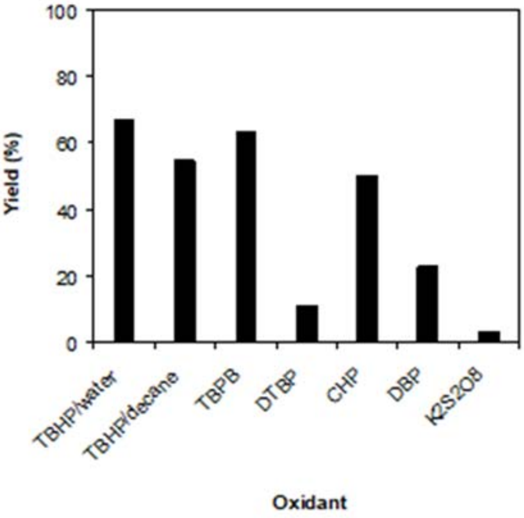

Fig. 9: Effect of oxidant on o-(2-benzothiazolyl)phenyl diethylcarbamate yield

One more question that must be scrutinized for reaction between of 2-(2-hydroxyphenyl) benzothiazole and DEF utilizing the magnetic nano catalyst is the required catalyst quantity. In the previous instance of the copper-catalyzed preparation of carbamates from dialkylformamides and phenols possessing benzothiazole directing substituents, Ali *et al.* (2015) employed 5 mol% copper acetate as catalyst for the reaction. The reaction was subsequently performed at 100ºC for 60 mins, utilizing 4 equivalents of aqueous *t*BuOOH oxidant, with 38 equivalents of DEF, in the presence of 0.5 mol%, 1 mol%, 3 mol%, 5 mol%, 7 mol%, and 10 mol% catalyst, respectively. The experimental outcome disclosed that only 10% yield was recognized after 60 mins for the reaction using 0.5 mol% catalyst. As anticipated, raising the catalyst amount caused a pronounced betterment in the yield of the expected product. The reaction utilizing 1 mol% catalyst provided 57% yield after 60 mins, while 61% yield was noted for that employing 3 mol% catalyst. The yield of *o*-(2-benzothiazolyl)phenyl diethylcarbamate could be mended to 67% after 60 mins in the presence of 5 mol% catalyst. Applying more than 5 mol% catalyst for the conversion was recognized to be not a good option as the final yield of the carbamate was not increased any more. It must be mentioned that no evidence of product was detected in the absence of the catalyst, proving the demand of the superparamagnetic nanoparticle catalyst for the reaction (Fig. 8).

Analogous to different transformations by C-H bond activation, the attendance of an oxidant must be demanded for the reaction between of 2-(2-hydroxyphenyl) benzothiazole and DEF. Next, the influence of different oxidants on the reaction yield was explored. The reaction was conducted at 100°C for 60 mins, employing 38 equivalents of DEF, in the presence of 5 mol% catalyst, with 4 equivalents of potassium persulfate, dibenzoyl peroxide, di-*tert*-butyl peroxide, *t*BuOOH in water, *t*BuOOH in decane, cumyl hydroperoxide, and *tert*-butyl peroxybenzoate, respectively, as the oxidant. Potassium persulfate, di-*tert*-butyl peroxide, and dibenzoyl peroxide should not be employed for the conversion. The reaction could continue to 50% yield after 60 mins in the attendance of cumyl hydroperoxide, dibenzoyl peroxide, while this number could be polished to 55% for the instance of *t*BuOOH in decane. The reaction utilizing *tert*-butyl peroxybenzoate could afford 63% yield after 60 mins. In the midst of these oxidants, *t*BuOOH in water emerged as the most desirable oxidant, providing 67% yield of *o*-(2-benzothiazolyl)phenyl diethylcarbamate after 60 mins (Fig. 9). Furthermore, it was spotted that the quantity of the oxidant also manipulated the formation of *o*-(2-benzothiazolyl)phenyl diethylcarbamate. Less than 3% yield was noted after 60 mins in the absence of the oxidant. Employing 1 equivalent of *t*BuOOH in water, the reaction could offer 71% yield of the anticipated product after 60 mins (Fig. 10).

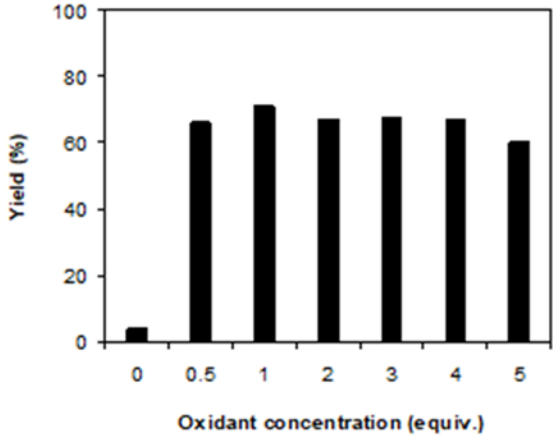

Fig. 10: Impact of oxidant concentration on o-(2-benzothiazolyl)phenyl diethylcarbamate yield

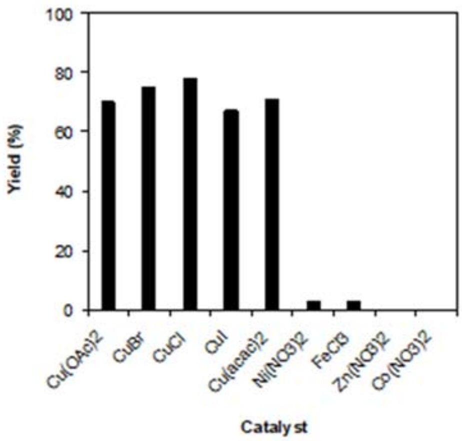

Fig. 11: Influence of different homogeneous catalysts on o-(2-benzothiazolyl)phenyl diethylcarbamate yield

The efficiency of the superparamagnetic nanoparticles was compared with diverse homogeneous catalysts in the reaction between 2-(2-hydroxyphenyl) benzothiazole and DEF. The reaction was conducted at 100°C for 120 min, deploying 1 equivalent of *t*BuOOH in water, utilizing and 38 equivalents of DEF, in the existence of 5 mol% catalyst. All nickel nitrate, cobalt nitrate, zinc nitrate, and ion(III) chloride displayed almost no catalytic activity for the conversion, while various copper salts could be utilized as homogeneous catalysts for the reaction. The reaction employing copper acetate catalyst could provide 70% yield after 60 mins, while 67% yield was recognized for that utilizing CuI catalyst. It was feasible to upgrade the reaction yield to 71% for the reaction using copper(II) acetylacetonate catalyst. CuBr and CuCl displayed higher catalytic activity, affording the expected product in 75% and 78% yields after 60 mins (Fig. 11). To underscore the impressive points of the superparamagnetic nanoparticles for this reaction, the activity of CuFe$_2$O$_4$ was also correlated to other nano catalysts. The experimental consequence suggested that copper species should be compulsory for the preparation of *o*-(2-benzothiazolyl) phenyl diethylcarbamate. The reaction utilizing CuO nano catalyst afforded 58% yield after 60 mins, while this figure could be amended to 63% for the case of Cu$_2$O nano catalyst. Deploying Cu nanoparticles, the yield could be upgraded to 69% after 60 mins. CuFe$_2$O$_4$ nanoparticles exhibited better representation, with 71% yield of the expected product being recognized after 60 mins (Fig. 12).

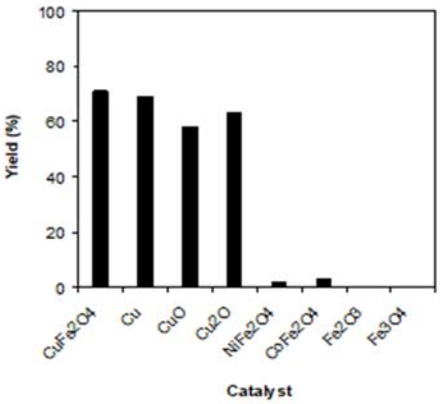

Fig. 12: Effect of various nano catalysts on o-(2-benzothiazolyl)phenyl diethylcarbamate yield

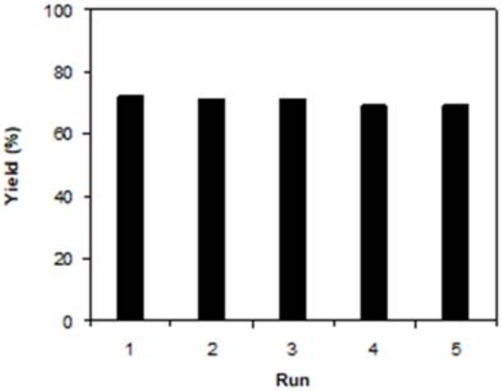

Fig. 13: Reutilization of catalyst

In the attitude towards green chemistry, the question should be answered when utilizing the superparamagnetic nanoparticles as catalyst for the reaction between 2-(2-hydroxyphenyl) benzothiazole and DEF should be its reusability. Despite the fact that abundant copper salts expressed high activity, it was impossible to recover them without a problematic approach. The magnetic nano catalyst was accordingly probed for reusability in the reaction over 9 sequent runs. The reaction was conducted at 100°C for 120 mins, deploying 1 equivalent of *t*BuOOH in water, employing 38 equivalents of DEF, in the existence of 5 mol% catalyst. Subsequent to the first run, the catalyst was gathered by magnetic decantation, washed carefully with DEF and methanol, dried at 150°C in a Shlenkline under vacuum for 6 hrs., and reused in new run. Data disclosed that that it was practicable to reutilize the catalyst for the reaction between 2-(2-hydroxyphenyl) benzothiazole and DEF without a conspicuous decline in efficiency. Positively, 69% yield of the expected product was still achieved in the 5th run (Fig. 13).

4 CONCLUSIONS

Superparamagnetic copper ferrite nanoparticles were utilized as a recyclable heterogeneous catalyst for the reaction between 2-(2-hydroxyphenyl) benzothiazole and DEF to produce *o*-(2-benzothiazolyl)phenyl diethylcarbamate as the major product. In this protocol, the benzothiazole acts as a directing substituent, facilitating the cross-dehydrogenative coupling conversion. This routine allowed the creation of a hybrid benzothiazole-carbamate moiety under heterogeneous catalysis. These products possess both carbamate and benzothiazole moieties, thus taking profits from both structures with regard to pharmaceutical and biological activities. Employing a catalytic portion of the nanoparticles, *o*-(2-benzothiazolyl)phenyl diethylcarbamate could be produced with reasonable yields within 2 hrs. It was practicable to recover the nanoparticles by magnetic separation, and reutilize them for the reaction without a significant decline in catalytic efficiency. The fact that hybrid benzothiazole-carbamate structures could be produced by utilizing a commercially available catalyst and that the catalyst could be recycled and reused would be interested to the chemical industry.

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