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A green, efficient and recyclable poly(4-vinylpyridine)-supported copper iodide catalyst for the synthesis of coumarin derivatives under solvent-free conditions

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ABSTRACT

Poly(4-vinylpyridine)-supported copper iodide is reported as a green, efficient and recyclable catalyst for the synthesis of coumarin derivatives by the Pechmann reaction under solvent-free conditions. This catalyst can be recovered by simple filtration and recycled up to eight consecutive runs without any loss of their efficiency.

1. Introduction

Coumarin derivatives are an important class of compounds that received significant attention from many pharmaceutical and organic chemists because of the broad spectrum of their biological and pharmaceutical properties such as antibacterial [1], anticancer [2] and inhibitory of HIV-1 protease [3]. Furthermore, these compounds are used as additives in food, perfumes, agrochemicals, cosmetics, pharmaceutical and in laser technologies due to their useful spectroscopic properties [4]. Several synthetic methods, like Pechmann condensation, Perkin, Reformatsky Wittig reaction, Knoevenagel condensation and Claisen rearrangement have been investigated for the synthesis of coumarins [5–8], of which the Pechmann reaction is the most common procedure. Therefore, various catalysts have been developed to improve the Pechman condensation [9–19]. In the past recent CuI is emerging as an effective Lewis acid catalyst for various organic transformations [20–25]. However, CuI has limitations such as thermodynamic instability, long reaction times, non-recyclable, toxicity and difficulty in separation of the product from the reaction medium. Such drawbacks could be obviated by using the supported catalyst. Nitrogen-based polymers have been shown to protect the metal center from oxidation and disproportionation, while enhancing its catalytic activity [26,27]. To improve the recovery and reuse, copper species have been immobilized on various supports such as carbon [28], amine-functionalized polymers [29], zeolites [30], amine-functionalized silica [31] and aluminum oxyhydroxide fiber [32]. Polymer-supported reagents have more and more attracted attention as insoluble matrices in organic synthesis [33]. They recommend rewards such as reaction monitoring as well as improved safety, more than ever when the non-supported reagents are toxic or unsafe as they can be easily removed from the reaction medium and recycled [34]. In addition, employing an excess amount of

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Table 1
Synthesis of coumarin derivatives catalyzed by P4VPy-CuI.

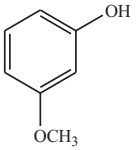
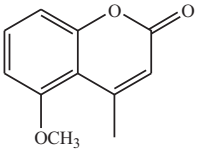
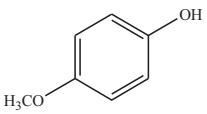
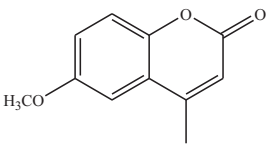
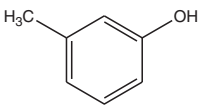
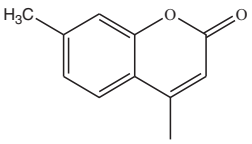
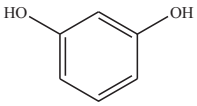
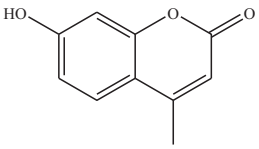
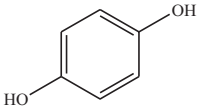
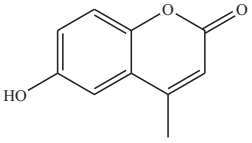
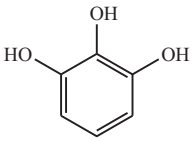
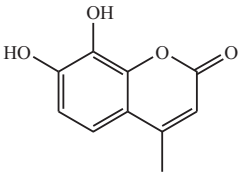
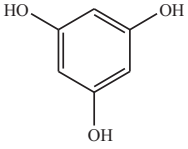
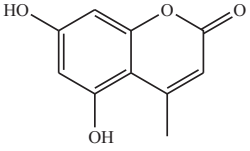
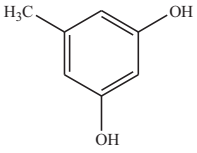
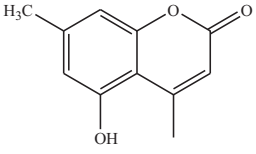
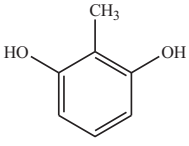
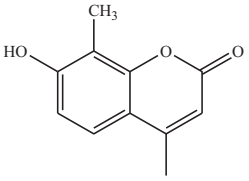
Entry	Phenol	Product	R^2	Time (min)	Yield (%)[a]	M.P. °C	
						Found	Reported [34]
1			Et	15	92	159–160	159–161
2			Et	30	88	169–171	169–170
3			Et	90	88	130–132	131–133
4			Et	10	89	184–185	184–186
5			Et	30	87	245–246	245–247
6			Et	12	90	242–244	242–244
7			Et	10	92	279–281	280–281
8			Et	10	90	259–260	258–259
9			Et	12	90	139–140	138–140

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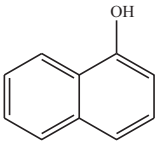
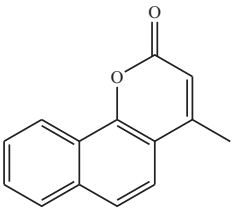
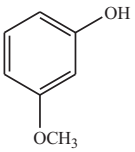
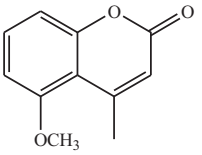
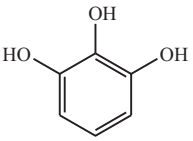
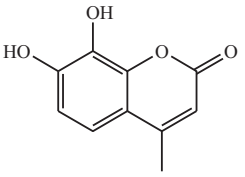
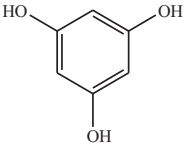
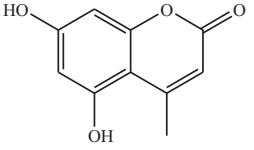
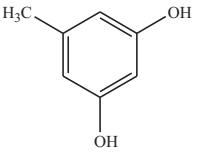
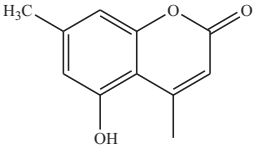
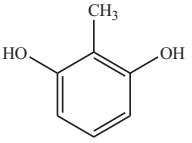
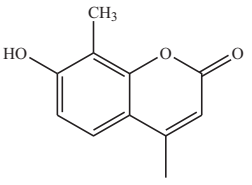
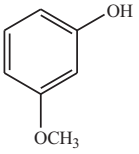
Table 1 (*Continued*)

Entry	Phenol	Product	R^2	Time (min)	Yield (%)[a]	M.P. °C	
						Found	Reported [34]
10			Et	35	84	155–157	156–157
11			Me	15	90	159–160	159–161
12			Me	15	89	242–244	242–244
13			Me	10	90	279–281	280–281
14			Me	10	89	259–260	258–259
15			Me	15	87	139–140	138–140
16		–	Me	120	–	–	–

Products were identified spectroscopically.
[a] Isolated yields.

reagent is allowed without the need for additional purification. Poly(4-vinylpyridine)-supported reagents are active for the various organic reactions including oxidations, reductions and halogenations. Simple recovery from reaction mixtures, their reusability, compatibility with a wide range of solvents, physical stability, and their toleration of a great number of reaction conditions bodes well for the future of P_4VPy-supported reagents in which their properties can be fine-tuned for specific chemical transformations [35]. Considering the above reports, and in continuation of our research on the synthesis of coumarins derivatives [36], herein, we wish to report a green, efficient and recyclable catalyst system based on Cu(I) particles supported on poly(4-vinylpyridine) (P_4VPy-CuI) for the synthesis of the coumarin derivatives by the Pechman reaction under solvent-free conditions.

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2. Experimental

Chemicals were purchased from Fluka, Merck and Aldrich Chemical companies. Products were characterized by comparison of their spectroscopic data (NMR, IR) and physical properties with those reported in the literature. All yields refer to isolated products. P_4VPy-CuI was prepared according to our previous articles [37,38].

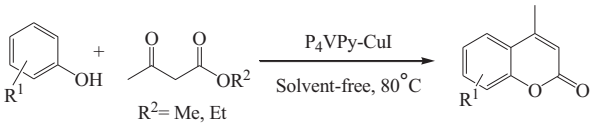
2.1. General procedure

A mixture of the phenol (1 mmol), ethyl acetoacetate or methyl acetoacetate (1 mmol) and poly(4-vinylpyridine)-CuI (0.1 g) was heated in an oil bath (80 °C) for the appropriate times according to Table 1. The progress of the reaction was monitored by TLC. After completion, the mixture reaction was allowed to cool, ethyl acetate (5 mL) was added and the catalyst was recovered to use subsequently by filtration. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol (0.83–0.91 mmol) afforded the pure products in high yields.

3. Results and discussion

The copper(I) iodide immobilized on poly(4-vinylpyridine) was readily prepared in a one-step procedure. Poly(4-vinylpyridine) was refluxed with a solution of CuI under N_2 atmosphere in EtOH for the synthesis of polymer-supported CuI particles. This method was developed for the effective synthesis of copper particles incorporated heterogeneously as catalyst in some organic reactions [39]. At first, for the optimization of the reaction conditions, a mixture of 3-methoxy phenol and ethyl acetoacetate was investigated as a model and its behavior was studied under a variety of conditions. The best result was achieved by caring out the reaction of 3-methoxy phenol and ethyl acetoacetate (with 1: 1 mol ratio) in the presence of 0.1 g of P_4VPy-CuI at 80 °C under solvent-free conditions (Table 1, entry 1). Using these optimized conditions, the reaction of other phenolic substrates with β-ketonic esters was explored (Scheme 1).

As shown in Table 1, all substrates were efficiently converted to their corresponding coumarins in good to high yields during short reaction times. All the products were cleanly isolated with simple filtration and evaporation of solvent. The solid products were easily recrystallized in hot ethanol. Among the various phenols studied, compounds containing electron donating were found to be most reactive and converted to their corresponding coumarins under the same reaction conditions. When the reaction was performed on phenols with electron-withdrawing groups, starting materials remain intact



Scheme 1. Synthesis of coumarin derivatives catalyzed by P_4VPy-CuI.

Table 2
Recyclability of P4VPy-CuI.

Run	1	2	3	4	5	6	7	8
Time (min)	15	15	15	17	20	20	20	25
Yield (%)[a]	92	92	89	89	88	88	85	82

[a] Isolated yields.

event after prolonged heating (Table 1, entry 16). The experimental procedure with this catalyst is very simple and the catalyst can be recovered easily by filtration. Very low amount of the catalyst (0.1 gr) and ethyl acetoacetate or methyl acetoacetate (1 mmol) is needed. This catalyst is cheap, easy to handle and its preparation is simple and straightforward. Moreover, our procedure is environmentally friendly as it does not use any toxic auxiliary or solvent. The activity of the recovered catalyst was also examined under the optimized conditions and the desired product was obtained in high yields after one to eight runs (Table 2). To investigate these properties for our introduced catalyst, the reaction of 3-methoxy phenol and ethyl acetoacetate was selected as the model (Table 2). After reaction completion, P_4VPy-CuI was washed with ethylacetate, dried and stored for another consecutive reaction run. This process was repeated for eight runs and no appreciable yield decrease was observed. Next we checked the leaching of CuI into the reaction mixture from the poly(4-vinylpyridine) support using ICP-AES. The difference between the copper content of the fresh and reused catalyst (8th run) is only 3% which indicates the low leaching amount of copper iodide catalyst into the reaction mixture.

4. Conclusion

In conclusion, we have developed a green and efficient procedure for the synthesis of coumarin derivatives by the Pechmann reaction catalyzed by P_4VPy-CuI under solvent-free conditions. This catalytic system is stable and can promote the yields and reaction times over eight runs without any loss of activity. Moreover, heterogeneous reaction conditions, high yields of products, short reaction times, ease of work-up and clean procedure will make this procedure a useful addition to the available methods. We are exploring further applications of P_4VPy-CuI for the other types of organic reactions in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.crci.2012.10.002.

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