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# (Carboxy-3-oxopropylamino)-3-propylsilylcellulose as an organocatalyst for the synthesis of coumarin derivatives under solvent-free conditions

**Mehri Salimi**

*Department of Chemistry, College of Sciences, University of Birjand, P.O. BOX 97175-615, Birjand, Iran*

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**Abstract**

In this research, (Carboxy-3-oxopropylamino)-3-propylsilylcellulose (COPAPSC), as an organocatalyst, has been synthesized by grafting of succinic anhydride on the -$NH_2$ modified cellulose (cellulose functionalized with 3-aminopropyltriethoxysilane). The –$CO_2H$ group-functionalized cellulose (COPAPSC) is used as a catalyst for the synthesis of coumarin derivatives from the reaction of phenolic substrate and β-ketoesters under solvent-free conditions. The results showed that the yield of products is between 85-94%. The advantages of this reaction include simple work-up, short reaction time, excellent yields as well as easily separation of the catalyst. The catalyst can be reused several times in subsequent reactions without any decreasing in the catalyst reactivity.

**Keywords:** (Carboxy-3-oxopropylamino)-3-propylsilylcellulose; solvent-free condition; Phenolic substrate; β-ketoester.

## Introduction

In the last two decades, science and technology have been devoted to the introduction and applications of environmentally friendly processes that minimize pollution and maximize sustainable development in chemical synthesis [1]. Preparing heterogeneous catalysts by immobilizing the homogenous precursors on a solid support is one of the important routes for developing novel heterogeneous

*Corresponding author: Mehri Salimi
Tel: +98 (56) 32202065, Fax: +98 (56) 32202065
E-mail: msalimi@birjand.ac.ir

catalysts. In almost all of these cases, the immobilized catalysts could provide advantages over their unsupported counterparts in terms of removal, recovery and reutilization of catalysts, reduced environmental contamination, moisture resistance, air tolerance, good thermal and chemical stabilities as well as good dispersion of the active catalytic sites [2, 3].

Various materials such as silica [4], zeolites [5], metal oxides [6], graphene [7], magnetic-materials [8] and polymers [9] have been broadly investigated to produce heterogeneous catalytic systems. The direction of science and technology has been shifting emphasis more on the sustainable resources and reusable catalysts. Thus, natural biopolymers such as gelatin [10], starch [11], chitosan [12], alginate [13] and cellulose derivatives [14] are attractive candidates to be used as solid supports for catalytic applications.

Among these bio-supports, cellulose which is the most abundant and inexhaustible biopolymer and renewable raw material in nature has unique properties as an organic support for the catalysts.

Coumarin and their derivatives which represent an important class of organic heterocyclic compounds have medical applications and can be found in many natural or synthetic drug molecules. They also possess versatile biological activities [15-17]. Coumarins have been extensively investigated because of their sufficient fluorescence in the visible light range, large stokes shift and high quantum yield [18, 19].

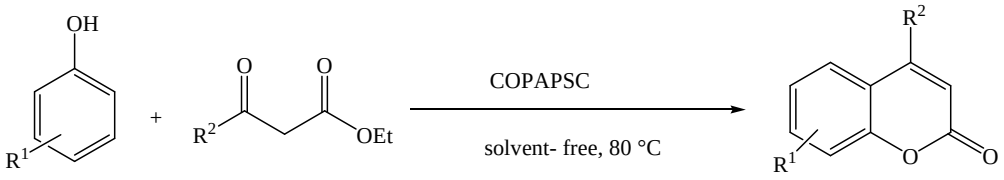
Plants are the most important natural source of coumarins, but the extraction of coumarins from plant is tedious, time consuming and needs more elaborate setup. Therefore, many synthetic methods, including Pechmann and Knoevenagol condensation [20, 21], Clisen rearrangement [22] and Wittig, Perkin and Reformatsky reactions [23-25] have been developed for the synthesis of coumarins. Pechmann condensation has been the most widely applied procedure, since it proceeds from simple starting materials (phenol and $\beta$-ketoester) through an acid catalyzed and producing high yields. Generally, concentrated sulfuric acid, trifluroacetic acid and phosphorous pentoxide [20, 26 and 27] are used as catalyst for the synthesis of coumarin and their derivatives.

Moreover, uses of other different homogeneous catalysts like Lewis acids and sulfonic acid were reported as acid catalysts for the Pechmann condensation reaction [28–32]. However, most of these acid catalysts are required in stoichiometric amounts to obtain high yield which caused their corrosiveness, difficulty in separation and creating severe environmental problems regarding disposal of post reaction wastes.

To address the above inherent limitations of homogeneous systems, a diverse array of supported catalysts and solid acids such as resins [33], Montmorillonite clay [34], nafion resin/silica composite [35], amberlyst ion-exchange resins [36], Periodic mesoporous silica Chloride [37], nano-crystalline sulfated-zirconia [38], benzylsulfonic acid functionalized mesoporous Zr-TMS [39], sulfonic acid nanoreactor [40], Alum ($KAl(SO_4)_2$ - $12H_2O$) [41] Polyvinylpolypyrrolidone-bound boron trifluoride ($PVPP\text{-}BF_3$) [42], Polyaniline-sulfate salts [43] and Mesoporous zirconium phosphate [44] have been developed by several groups to catalyze the pechmann reaction with different degrees of success. However, these protocols do not always lead to satisfactory results and they generally require longer reaction times and higher reaction temperatures than the homogeneous catalyst systems.

Therefore, it seems that there is still much room to develop new methods based on recyclable catalysts under more appropriate reaction conditions.

From this discussion and our interest and experience in the area of heterogeneous catalysis in organic synthesis [45–49], we prepared COPAPSC according to the previously reported procedure [49] and used for the synthesis of coumarin from the mixture of phenol and β-ketoester under solvent-free condition (Scheme 1).




**Scheme 1.** Synthesis of 4-substituted coumarins using COPAPSC

## Experimental

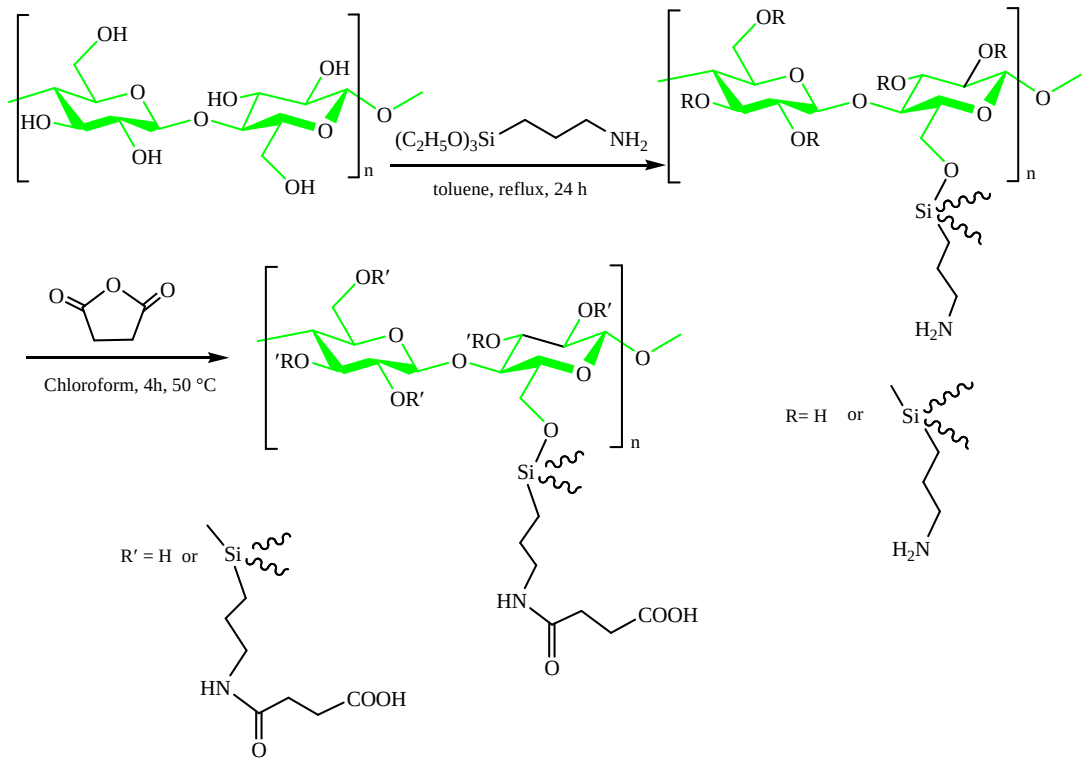
*General*

Chemicals were purchased from Merck and Fluka chemical companies. IR spectra were obtained in KBr pellets in the reflection mode on an Avata Therma Nicolet FT-IR instrument.

$^{1}$H NMR spectra were obtained on a Bruker Avance DPX-250 MHz spectrometer using TMS as an internal standard and $CDCl_3$ or DMSO as the solvent. $^{13}$C NMR spectra were obtained on a Bruker Avance DPX-62.5 MHz spectrometer ($CDCl_3$ or DMSO solvent). Mass spectra were obtained on a GC-17A, MS QP-5050 Shimadzu instrument. All the reactions were monitored by thin layer chromatography (TLC) on pre-coated sheets of silica gel G/UV-254 using UV light for visualization. Melting points were determined with an Electrothermal 9100 melting point apparatus.

## Preparation of COPAPSC

A magnetically stirred cellulose (5.0 g) was suspended in dry toluene (50 mL) followed by addition of 3-aminopropyltriethoxysilane (3-APTES, 5.0 mL). The suspension was heated under reflux for 24 h under inert atmosphere. The resulting white solid was filtered, washed repeatedly with toluene, ethanol–water, deionized water and methanol and dried under vacuum at 60 °C for 4 h to give 3-aminopropylsilylcellulose (3-APSC, 5.2 g). This 3-APSC functionalized cellulose was stirred with 0.15 g (15 mmol) of succinic anhydride dissolved in dry chloroform (20 mL) for 4 h at 50 °C and the final product was collected by filtration, washed sequentially with chloroform, ethanol and diethyl ether. The product was dried in vacuum desiccator to give COPAPSC as a white powder (5.23 g) (Scheme 2).




**Scheme 2.** Preparation of (carboxy-3-oxopropylamino)-3-propylsilylcellulose

**General procedure for the synthesis of 4-substituted coumarins**

To the mixture of phenolic substrate (1 mmol) and β-ketoesters (1 mmol), COPAPSC (0.2 g equals to 0.044 mmol of $H^+$) was added and magnetically stirred at 85 °C. The progress of the reaction was followed by TLC. After the completion of the reaction, warm ethanol (2×10 mL) was added and the mixture stirred for 5 min and filtered. Ethanol was evaporated under reduced pressure and crude product was recrystallized from hot ethanol. The recovered catalyst was dried and reused.

**Results and discussion**

*Catalyst characterization*

Figure 1 shows the FT-IR spectra of cellulose and COPAPSC. The band at around 3200–3500 $cm^{-1}$ range is attributed to the O–H and N–H stretching vibrations of COPAPSC. The observed peaks at 1419, 1058, 1203 and around 2933–2898 $cm^{-1}$ in the FT-IR spectrum of COPAPSC corresponded to C–N, C-O, Si-C and C–H stretching modes of the alkyl chain, respectively.

The bands at 1728 and 1693 $cm^{-1}$ are attributed to the carbonyl groups of acid and amide, respectively [14]. The O-H vibration of the carboxylic groups was overlapped with the O-H vibration of cellulose.

The nitrogen content in COPAPSC was determined to be 0.32% (0.23 mmol $g^{-1}$) by elemental analysis. The number of $H^+$ sites of COPAPSC was determined to be 0.22 mmol $g^{-1}$ by an acid–base titration, which was very close to the nitrogen content. These results indicated that most of the nitrogen species on the sample were in the form of amide groups.

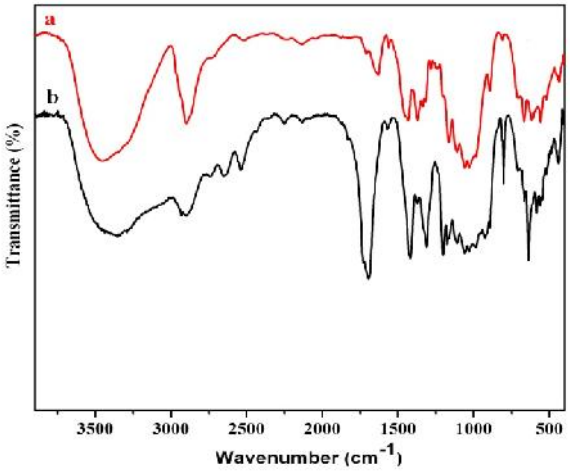
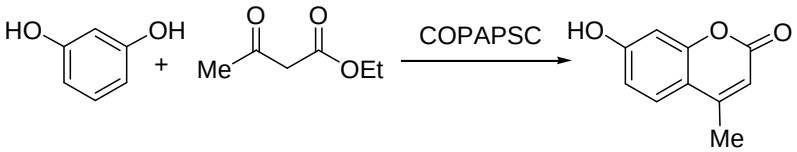



**Figure 1.** FT-IR spectra of: (a) cellulose and (b) COPAPSC

In continuation of our work on the development of novel synthetic methodologies toward the synthesis of heterocyclic compounds, the catalytic activity of COPAPSC was tested for the synthesis of coumarin derivatives. We studied COPAPSC as a catalyst in the cyclo-condensation of phenol and β-ketoester. Firstly, the reaction of resorcinol (1 mmol) and ethyl acetoacetate (1 mmol) was investigated in different solvents as well as under solvent-free conditions in the presence of COPAPSC as catalyst and the results are shown in Table 1.

**Table 1.** Effect of solvent, temperature and the amount of catalyst on the synthesis of **3a**[a]



| Entry | Catalyst (g) | Solvent | Temperature (°C) | Time (min) | Yield [b] (%) |
|---|---|---|---|---|---|
| **1** | Cellulose (0.2) | Solvent-free | 85 | 120 | 5 |
| **2** | COPAPSA (0.08) | Solvent-free | 65 | 60 | 40 |
| **3** | COPAPSA (0.10) | Solvent-free | 65 | 60 | 52 |
| **4** | COPAPSA (0.20) | Solvent-free | 65 | 60 | 63 |
| **5** | COPAPSA (0.08) | Solvent-free | 75 | 60 | 55 |
| **6** | COPAPSA (0.10) | Solvent-free | 75 | 52 | 73 |
| **7** | COPAPSA (0.20) | Solvent-free | 75 | 55 | 80 |
| **8** | COPAPSA (0.08) | Solvent-free | 85 | 40 | 60 |
| **9** | COPAPSA (0.10) | Solvent-free | 85 | 35 | 72 |
| **10** | COPAPSA ( 0.2) | Solvent-free | 85 | 30 | 94 |
| **11** | COPAPSA (0.3) | Solvent-free | 85 | 30 | 94 |
| **12** | COPAPSA (0.20) | Water | 85 | 60 | - |
| **13** | COPAPSA (0.20) | Methanol | reflux | 60 | 15 |
| **14** | COPAPSA (0.20) | Ethanol | reflux | 60 | 10 |
| **15** | COPAPSA (0.20) | Dichloromethan | reflux | 60 | - |
| **16** | COPAPSA (0.20) | ethyl acetate | reflux | 60 | 10 |

[a]Reaction condition: resorcinol (1 mmol) and ethyl acetoacetate (1 mmol) in the presence of cellulose and COPAPSA
[b]Isolated yields

Initial screening studies confirmed that the solvent-free technique is the optimal condition for this reaction. Another important point which could be obtained evidently from these results is that raising the reaction temperature from 60 to 85 °C and the amount of catalyst from 0.08 to 0.2 g increased the yield and also improved the reaction rates (Table 1, Entries 2–10). A further increase in the catalyst loading does not affect the yield (Table 1, Entry 11). Moreover, it is worth mentioning that application of solvents, such as $H_2O$, EtOH, MeOH, EtOAC and $CH_2Cl_2$ did not improve the yields. Under these

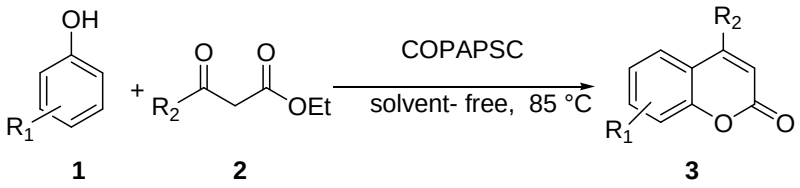
conditions, longer reaction times and lower yields can be observed (Table 1, Entries 12–16). On the contrary, a great amount of waste is attributed to the use of organic solvents in the environment. Therefore, organic reactions without the use of conventional organic solvents have attracted the attention of synthetic organic chemists. The development of solvent-free organic reactions is thus gaining prominence.

Also, cyclocondensation of resorcinol and ethylacetoacetate was carried out with bare cellulose as catalyst at 85 °C for 2 h under solvent-free conditions which resulted in a yield of 5-6% (Table 1, Entry 1).

The efficiency of COPAPSC was demonstrated by synthesizing dozen of coumarins using a series of monohydric and polyhydric phenols with β-ketoesters under the optimum conditions (Table 2). The proposed catalyst was found to be effective for the reactions of phenols bearing either electron-donating (Table 2, Entries 4-7) or electron-withdrawing substituents with β-ketoesters (Table 2, Entry 8). The present method is superior to the previously reported methods regarding yields and reaction time [28, 30].

The efficiency of our method for the synthesis of coumarin is compared with some other published works in the literature (Table 3). The reaction of resorcinol with ethyl acetoacetate was used as a model reaction. Each of these reported methods have their own advantages, but they often suffer from some drawbacks including the use of organic solvent (Entry 6), longer reaction times (Entries 2–8) and use of Lewis acid (Entries 10–12).

**Table 2.** Synthesis of coumarins *via* Pechmann condensations of phenols with β-ketoester catalyzed by COPAPSC[a]




**1** **2** **3**

| Entry | $R^1$ | $R^2$ | Product | Time (min) | M.p. °C (lit.) [Ref.] | Yield(%)[b] |
|---|---|---|---|---|---|---|
| **1** | 3-OH | $CH_3$ | 3a | 30 | 185 185-187 [31] | 94 |
| **2** | 2,6-$(OH)_2$ | $CH_3$ | 3b | 25 | 240-242 236-239[31] | 92 |
| **3** | 3,5-$(OH)_2$ | $CH_3$ | 3c | 25 | 281-283 281-283[31] | 93 |
| **4** | 3-Me-5-OH | $CH_3$ | 3d | 40 | 251-253 256-258 [31] | 92 |
| **5** | 2-Me-3-OH | $CH_3$ | 3e | 45 | 261 263-265 [32] | 93 |
| **6** | 3-MeO | $CH_3$ | 3f | 60 | 158-160 160-162 [31] | 87 |
| **7** | 6-MeO-3-OH | $CH_3$ | 3g | 60 | 159-163 163-164[31] | 90 |
| **8** | 4-$NO_2$ | $CH_3$ | 3h | 60 | 147-149 151-154[31] | 85 |
| **9** | 3,5-$(OH)_2$ | $CF_3$ | 3j | 20 | 250-252 250-252 [28] | 94 |
| **10** | 3-OH-4-Cl | $CH_3$ | 3k | 90 | 285-288 285-286 [26] | 90 |
| **11** | 1-naphtol | $CH_3$ | 3m | 120 | 153-155 154-156 [31] | 88 |

[a]Reactions were performed with phenol (1.0 mmol), β-ketoester (1.0 mmol), COPAPSA (0.2 g) as catalyst at 85 °C under solvent-free conditions.
[b]Isolated yields of pure products

**Table 3.** Comparison of the efficiency of COPAPSC with different catalysts

| Entry | Catalyst | Reaction condition | Yield (%) | [Ref.] |
|---|---|---|---|---|
| **1** | Sulfonic acid nanoreactor | Solvent-free, 130 °C, 60 min | 90 | [40] |
| **2** | Alum ($KAl(SO_4)_2$ - $H_2O$) | Solvent-free, 80 °C, 2 h | 92 | [41] |
| **3** | PVPP-$BF_3$ | EtOH, reflux, 2 h | 91 | [42] |
| **4** | Polyaniline-sulfate salts | Solvent-free, 150 °C, 6 h | 70 | [43] |
| **5** | nano-crystalline sulfated-zirconia | Solvent-free, 170 °C, 3 h | 78 | [38] |

| | | | | |
|---|---|---|---|---|
| **6** | Mesoporous zirconium phosphate | Solvent-free, 150 $^{o}$C, 4 h | 76 | [44] |
| **7** | Zr-TMS-BSA | Solvent-free, 150 $^{o}$C, 20 h | 75 | [39] |
| **8** | Periodic mesoporous silica Chloride | Solvent-free, 130 $^{o}$C, 60 min | 94 | [37] |
| **9** | $Bi(NO_3)_3$. $5H_2O$ | Solvent-free, 150 $^{o}$C, 20 min | 92 | [32] |
| **10** | $TiCl_4$ | Solvent-free, r.t, 60 min | 97 | [28] |
| **11** | $Sm(NO_3)_3.6H_2O$ | Solvent-free, 80 $^{o}$C, 20 min | 98 | [31] |
| **12** | COPAPSC | Solvent-free, 80 $^{o}$C, 30 min | 94 | This work |

The proposed mechanism for the formation of the product could be explained by the pathway presented in Figure 2. The reaction commenced through the acid catalyzed protonation of ethyl acetoacetate (**2**) has underwent nucleophilic attack by resorcinol to give intermediate **4**, which is prortonated by COPAPSC (intermediate **5**), followed by dehydration (intermediate **6**). Finally, cyclization occurred and coumarin was formed (**3a**) [43].

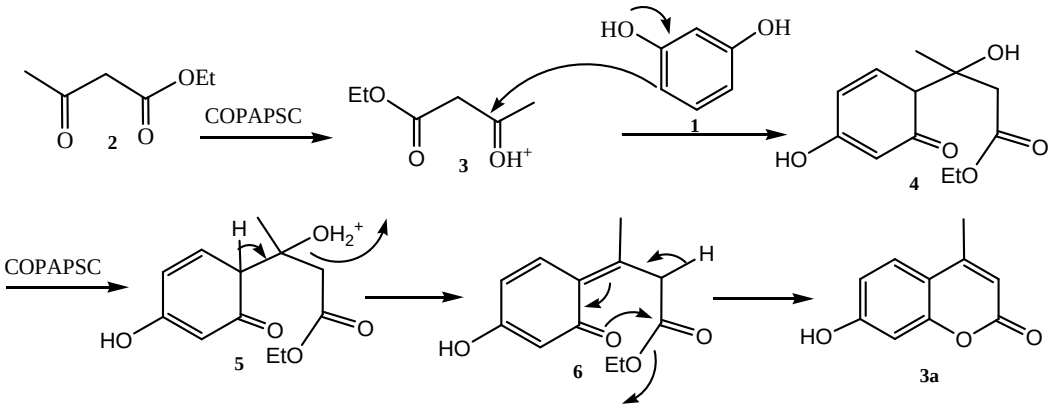



**Figure 2.** Probable mechanism for the formation of 3a using COPAPSC as catalyst

The recyclability of the catalyst was also examined. After the completion of the first run to afford the corresponding coumarin in 94% yield, the catalyst was thoroughly washed with warm EtOH and dried at 80 $^{o}$C for

4 h. A new reaction was designed with fresh resorcinol and ethyl acetoacetate under the same reaction conditions. The recovered catalyst was successfully used in 4 consecutive runs, exhibiting consistent activity to afford an average yield of 88% with virtually no significant loss of performance. The results with the recyclable COPAPSC are summarized in figure 3.

**Conclusion**

In summary, we have implemented COPAPSC as an efficient, reusable, green and solidly supportive acid catalyst for the synthesis of coumarin derivatives by cyclo-condensation reaction of phenolic substrates with β-ketoesters. The broad scope, operational simplicity and practicability render it as an attractive approach for the producing of different coumarin derivatives with potential use in biologically important compounds.

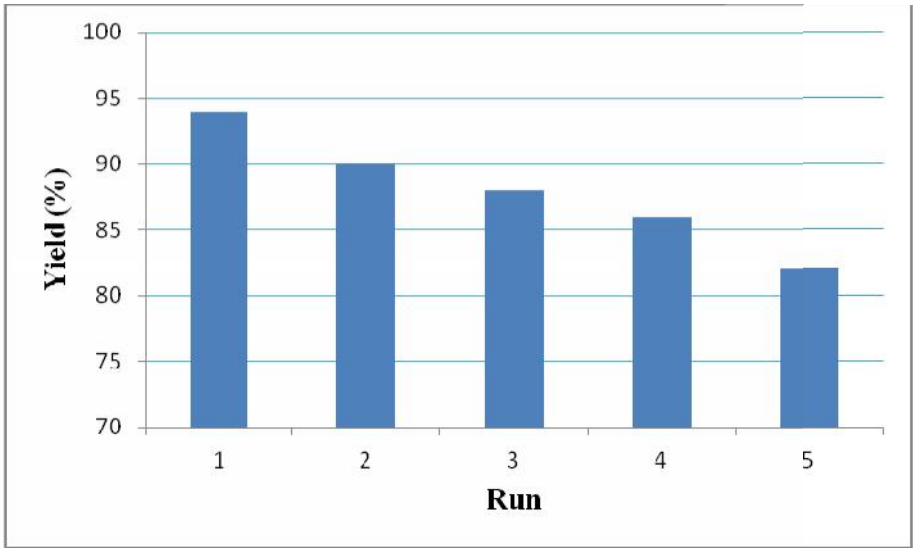



**Figure 3.** Reusability of COPAPSC in the cyclo-condensation of resorcinol and ethyl acetoacetate at 85 °C under solvent-free conditions in 30 min

**Acknowledgments**

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**References**

[1] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.M. Basset, *Chem. Rev*., **2011**, *111*, 3036–3075.

[2] S.E. Garc´ıa-Garrido, J. Francos, V. Cadierno, J.M. Basset V. Polshettiwar, *Chem. Sus. Chem.*, **2011**, *4*, 104–111.

[3] (a) H.U. Blaser, A. Baiker, R. Prins, *Heterogeneous catalysis and fine chemicals IV*, Elsevier, Netherlands, 1997; (b) J.M. Thomas and W.J. Thomas, *Principles and practice of heterogeneous catalysis*, VCH, Weinheim, **1997**.

[4] N. Audic, H. Clavier, M. Mauduit, J.C. Guillemin, *J. Am. Chem. Soc*., **2003**, *125*, 9248–9249.

[5] (a) L.J. Gu, D. Ma, S.D. Yao, C.L. Wang, W.J. Shen, X.H. Bao, *Chem. Commun*., **2010**, *46*, 1733–1735; (b) M. Iwasaki, H. Shinjoh, *Chem. Commun*., 2011, *47*, 3966–3968.

[6] E. Ortel, S. Sokolov, C. Zielke, L. Lauermann, S. Selve, K. Weh, B. Paul, J. Polte and R. Kraehnert, *Chem. Mater*., **2012**, *24*, 3828–3838.

[7] M. Yang, M. Zhou, A.H. Zhang, C. Zhang, *J. Phys. Chem. C*, **2012**, *116*, 22336–22340.

[8] R.B.N. Baig, R.S. Varma, *Chem. Commun*., **2012**, *48*, 2582–2584.

[9] R.B.N. Baig, R.S. Varma, *Green Chem*., **2013**, *15*, 1839–1843.

[10] H. Firouzabadi, N. Iranpoor, A. Ghaderi, *Org. Biomol. Chem*., **2011**, *9*, 865–871

[11] R.S. Verma, S.L. Jain, B. Sain, *Chem. Cat. Chem*., **2011**, *3*, 1329–1332.

[12] E. Guibal, *Prog. Polym. Sci*., **2005**, *30*, 71–109.

[13] M.Chtchigrovsky, Y. Lin, K. Ouchaou, M. Chaumontet, M. Robitzer, F. Quignard, F. Taran, *Chem. Mater*, **2012**, *24*, 1505–1510.

[14] H.Y. Yu, G.Y. Chen, Y.B. Wang, J.M. Yao, *Cellulose*, **2015**, *22*, 261–273.

[15] R.O. Kennedy, R.D. Thornes, Coumarins: Biology, *Applications and Mode of Action*, John Wiley and Sons, Chichester, **1997**.

[16] O. Snow, *Amphetamine syntheses*, *Psychoactive Synth. Ser*.: USA 1, 1998.

[17] S.M. Sethna, N.M. Shah, *Chem. Rev*. **1945**, *36*, 1–62.

[18] X.T. Liang, W.S. Fang, *Medicinal chemistry of bioactive natural products*, John Wiley & Sons: Hoboken, New Jersey, **2006**.

[19] G. Cavettos, G.M. Nano, G. Palmisano, S. Tagliapietra, *Tetrahedron-Asymmetry*, **2001**, *12*, 707–709.

[20] V.H Pechmann, C. Duisberg, *Chem. Ber*., **1884**, *17*, 929-979.

[21] G. Brufola, F. Fringuelli, O. Piematti, F. Pizzo, *Heterocycles*, **1996**, *43*, 1257-1266.

[22] N.Cairns, M.L. Harwood, D.P Astles, *J. Chem. Soc. Perkin Trans*, **1994**, *1*, 3101-3107.

[23] I. Yavari, R.R Hekmat-shoa, A. Zonouzi, *Tetrahedron Lett*., **1998**, *39*, 2391-2392.

[24] J.R. Johnson, *Org. React*., **1942**, *1*, 210-265.

[25] R.L Shriner, *Org. React*., **1942**, *1*, 1-37.

[26] L.L. Woods, J. Sapp, *J. Org. Chem*., **1962**, *27*, 3703-3705.

[27] F.W. Canter, F.H. Curd, A. Robertson, *J. Chem. Soc*. CLXVI.-Hydroxy-carbonyl compounds, Part III, **1931**, 1255-1265.

[28] H. Valizadeh, A. Shockravi, *Tetrahedron Lett*., **2005**, *46*, 3501-3503.

[29] P. Sun, Z. Hu, *Synth. Commun*., **2005**, *35*, 1875-1880.

[30] S.K. De, R.A. Gibbs, *Synthesis*, **2005**, 8, 1231–1233.

[31] V. M. Alexander, R. P. Bhat, S. D. Samant, *Tetrahedron Letters*, **2004**, *45*, 7999–8001.

[32] S. S. Bahekar, D. B. Shinde, *Tetrahedron Letters*, **2005**, *46*, 6957–6959.

[33] E.V.O. John, S.S. Israelstam, *J. Org. Chem*., **1961**, *26*, 240–242.

[34] T.S. Li, Z.H. Zhang, F. Yang, C.G. Fu, *J. Chem. Res*., **1998**, 38–39.

[35] M.C. Laufer, H. Hausmann, W.F. Hölderich, *J. Catal*., **2003**, *218*, 315–320.

[36] R. Sabou, W.F. Hoelderich, D. Ramprasad, R. Weinand, *J. Catal.*, **2005**, *232*, 34–37.

[37] B. Karimi, H. Behzadnia, *Catalysis Communications*, **2011**, *12*, 1432–1436.

[38] B. Tyagi, M.K. Mishra, R.V. Jasra, *J. Mol. Catal. A: Chem*., **2007**, *276*, 47–56.

[39] S. Selvakumar, M. Chidambaram, A.P. Singh, *Catal. Commun*., **2007**, *8*, 777–783.

[40] B. Karimi, D. Zareyee, *Organic Leeters*, **2008**, *10*, 3989-3992.

[41] M. Dabiri, M. Baghbanzadeh, S. Kiani, Y. Vakilzadeh, *Monatshefte fur Chemie*, **2007**, *138*, 997–999.

[42] M. Mokhtary, F. Najafizadeh, *C. R. Chimie*, **2012**, *15*, 530–532.

[43] S. Palaniappan, R. C.Shekhar, *Journal of Molecular Catalysis A: Chemical*, **2004**, *209*, 117–124.

[44] A. Sinhamahapatra, N. Sutradhar, S. Pahari, H.C. Bajaj, A. B. Panda, *Applied Catalysis A: General*, **2011**,394, 93–100.

[45] M.A. Nasseri, M. Salimi, *Letters in Organic Chemistry*, **2013**, *10*, 164-170.

[46] M.A. Nasseri, A. Mohammadinezhad, M. Salimi *J. Iran, Chem. Soc*., **2015**, *12*, 81–86.

[47] A. Mohammadinezhad, M.A. Nasseri, M. Salimi, *RSC Adv*., **2014**, *4*, 39870–39874.

[48] M.A. Nasseri, M. Salimi, A.A. Esmaeili, *RSC Adv*., **2014**, *4*, 61193–61199.

[49] M. Salimi, M.A. Nasseri, T. Daliran Chapesshloo, B. Zakerinasab, *RSC Adv*., **2015**, *5*, 33974-33980.