# Coumarins: Facile and Expeditious Synthesis *via* Keggin-Type Heteropolycompounds under Solvent-Free Condition

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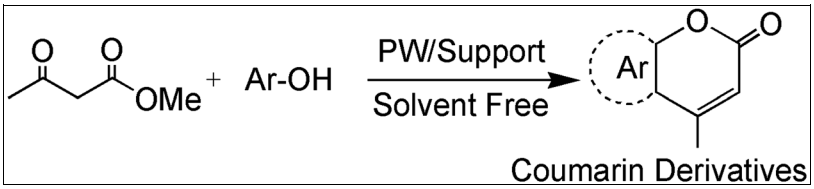


Different Keggin-type heteropolycompounds were used in Pechmann reaction to obtain biologically active coumarins. Effect of solvent, catalyst loading, and molar ratios of substrates was studied to introduce the best reaction condition. The optimized reaction condition was extended to Pechmann reaction of methylacetoacetate with various monohydric and polyhydric phenols. This rapid procedure afforded structurally diverse coumarins with high to excellent yields. Short reaction times, simple work-up, and mild reaction conditions were advantages of this method. The optimized catalysts were reusable for four runs.

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## INTRODUCTION

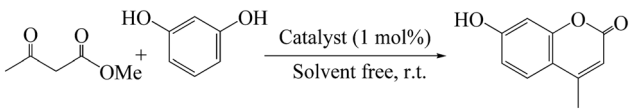
In recent years, there has been extensive effort to design novel protocols for synthesis of biologically important molecules using heterogeneous catalysts. Heterocyclic compounds are important constituents that often exist in biologically active natural products and synthetic compounds of medicinal interest. Among various heterocyclic compounds, coumarins have been widely studied because they are structural units of several natural products [1] and feature broadly in pharmacologically and biologically active compounds [2]. They are extensively used in the cosmetics, optical brightening agents [3], laser dyes [4], additives in food, perfume, and insecticides [2]. Also, they have varied bioactivities, for example, anticancer [5], anti-inflammatory [6], antiviral [7], anti-HIV [8], anticonvulsant [9], anticoagulant [10], antioxidant [11], antibacterial [12], antifungal [13], anticarcinogenic material [14], and as antihistamine [15]. Coumarins can be synthesized by various methods including the Perkin [16], Pechmann [17], Knovenagel [18], Reformatsky [19], and Wittig [20] reactions. Among these, the Pechmann reaction has been the most widely used method because it proceeds from very simple starting materials and gives good yields of variously substituted coumarins. In 1883, Pechmann described an efficient synthesis of coumarins by reacting phenols and β-ketoesters in the presence of sulfuric acid as a catalyst [17]. Conventionally, the Pechmann reaction is carried out in the presence of concentrated $H_2SO_4$, $P_2O_5$ [21], trifluoroacetic acid [22], and $AlCl_3$ [23]. These acids are corrosive and required in excess amount or long reaction time. Homogeneous metal chlorides such as $ZnCl_4$, $TiCl_4$, $InCl_3$, $GaI_3$ [24–27], triflates [28], sulfonic acid [29], and ionic liquids [30–33] are reported to produce coumarin derivatives. Because of nonreusability of these homogeneous catalysts, different solid acid catalysts such as Amberlyst ion-exchange resins [34], zeolites [35], [36], K-10 [37], polyaniline sulfate salt [38], [39], and nafion resin/silica nanocomposites [40] have been studied. Also, $KAl(SO_4)_2{\cdot}12H_2O$ [41], dipyridine copper chloride [42], and iodine [43] are used as catalyst for the synthesis of coumarin derivatives. However, some of mentioned catalysts suffer from either a tedious synthetic methodology or requirement of large amount of catalyst for high yield, high temperature often in the range of 100–150°C. Furthermore, in most of the cases, toluene has been used as a solvent. Also, some of the Lewis acids are moisture sensitive and require special care in handling and storage, and some of the mentioned catalysts such as triflates are highly expensive. Consequently, there is scope for further development of milder reaction conditions, using green and reusable catalysts and efficient methodology to synthesize these compounds and their derivatives.

Based on our recent success with the use of heteropolycompounds (HPCs) as a catalyst in organic transformations 44–46], our research group has been working in the preparation of these biologically important molecules by different kinds of Keggin-type HPCs under mild reaction condition.

## RESULTS AND DISCUSSION

To explore the catalytic activity of different Keggin-type catalysts in Pechmann reaction, methylacetoacetate and resorcinol were first chosen as a model reaction (Scheme 1).

**Scheme 1**




Positive results were obtained in the cases of $H_3PW_{12}O_{40}$ (PW), $H_3PMo_{12}O_{40}$ (PMo), $H_4SiW_{12}O_{40}$ (SiW), $K_5CoW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $[(n\text{-}C_4H_9)_4N]_3PMo_2W_9O_{39}$ ($M^{n+}{\cdot}xH_2O$), $M^{n+}$ = $Ti^{4+}$, $Sn^{4+}$, and $Zn^{4+}$. In other cases, no improvement in the yield was observed by prolonged reaction time (Table 1). PW gave a maximum yield in minimum time and hence was used for all other reaction.

The use of a support allowing the PW to be dispersed over a large surface must result in an increase of its catalytic activity. In this way, many studies have been done lately using a great variety of supports: silica, clay, alumina, carbon, *etc*. [47], [48]. Surface area enhancement, higher dispersion of acidic protons, heterogenization, and acid strength control are some of the goals for preparing supported HPCs. Activity of different supports only and supported PW has been checked in model reaction (Table 2). Higher yields than those obtained with other catalysts are achieved with the PW supported on silica, titania, and carbon (Table 2, entries 2, 6, and 12). It is an established fact in the literature that Pechmann reaction proceeds through transesterification and intramolecular hydroxylation, followed by dehydration [35], [49]. These three steps are all typical acid-catalyzed reactions. Therefore, the outcome of the Pechmann reaction depends very much on the acidity of the catalysts. Thus, the observed trend in activity of the supported catalyst (Table 2) may be related to the PW–support interaction, which in turn is associated to support properties and acidic strength of the acid sites. Surface area and $E_i$ (initial electrode potential that indicates the maximum strength of the acid sites), which have reported in our previously published article [50], are listed in Table 2. It was observed that the catalysts with high $E_i$ and surface area show high catalytic activity. PW/$\gamma$-$Al_2O_3$ shows less acidic property and it is not active in catalytic reaction (Table 2, entry 4). PW/KSF indicates high acidity but its surface area is very low. Thus, it seems that the catalytic activity of PW/support is correlated with total acidity and surface properties. Therefore, for many catalytic applications, the dispersion of PW onto a high surface area carrier is desirable. Based on these observations, the best catalysts among all are proposed.

**Table 1**

Activity of Different Catalysts in the Reaction of Methylacetoacetate with Resorcinol.

| Entry | Catalyst | Time (min) | Yield (%)[a] |
|---|---|---|---|
| 1 | $H_3PW_{12}O_{40}$ | 20 | 98 |
| 2 | $H_3PMo_{12}O_{40}$ | 25 | 95 |
| 3 | $H_4SiW_{12}O_{40}$ | 20 | 86 |
| 4 | $H_5PMo_{10}V_2O_{40}$ | 40 | No reaction |
| 5 | $H_6PMo_9V_3O_{40}$ | 40 | No reaction |
| 6 | $H_7PMo_8V_4O_{40}$ | 60 | No reaction |
| 7 | $K_7Ti_2W_{10}PO_{40}$ | 60 | No reaction |
| 8 | $K_5ZnTi_2W_{10}PO_{40}$ | 60 | No reaction |
| 9 | $K_5CoW_{12}O_{40}$ | 30 | 12 |
| 10 | $[(t\text{-}C_4H_9)_4N]_4PW_{11}CoO_{39}$ | 60 | No reaction |
| 11 | $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ | 40 | 14 |
| 12 | $[(n\text{-}C_4H_9)_4N]_5PMo_2W_9O_{39}$ ($Sn^{2+}{\cdot}H_2O$) | 60 | No reaction |
| 13 | $[(n\text{-}C_4H_9)_4N]_3PMo_2W_9O_{39}$ ($Sn^{4+}{\cdot}H_2O$) | 30 | 10 |
| 14 | $[(n\text{-}C_4H_9)_4N]_3PMo_2W_9O_{39}$ ($Ti^{4+}{\cdot}H_2O$) | 30 | 21 |
| 15 | $[(n\text{-}C_4H_9)_4N]_5PMo_2W_9O_{39}$ ($Zn^{2+}{\cdot}H_2O$) | 40 | 19 |

[a]Isolated yield.

**Table 2**

Surface Area, Acidic Strength, and Activity of Different Supports and Supported PW in the Reaction of Methylacetoacetate with Resorcinol.

| Entry | Catalyst | Time (min) | Yield (%)[a] | Surface area ($m^2\ g^{-1}$) | $E_i$ (mV) |
|---|---|---|---|---|---|
| 1 | $SiO_2$ | 60 | No reaction | | |
| 2 | 40 wt % PW/$SiO_2$ | 17 | 98 | 117 | 693 |
| 3 | $\gamma$-$Al_2O_3$ | 60 | No reaction | | |
| 4 | 40 wt % PW/$Al_2O_3$ | 60 | No reaction | 200 | 150.3 |
| 5 | $TiO_2$ | 65 | No reaction | | |
| 6 | 40 wt % PW/$TiO_2$ | 11 | 98 | 37 | 662 |
| 7 | KSF | 25 | 30 | | |
| 8 | 40 wt % PW/KSF | 25 | 35 | <5 | 540 |
| 9 | K10 | 60 | No reaction | | |
| 10 | 40 wt % PW/K10 | 35 | 71 | 82 | 530 |
| 11 | C | 60 | No reaction | | |
| 12 | 40 wt % PW/C | 20 | 96 | 272 | 686 |

[a]Isolated yield.

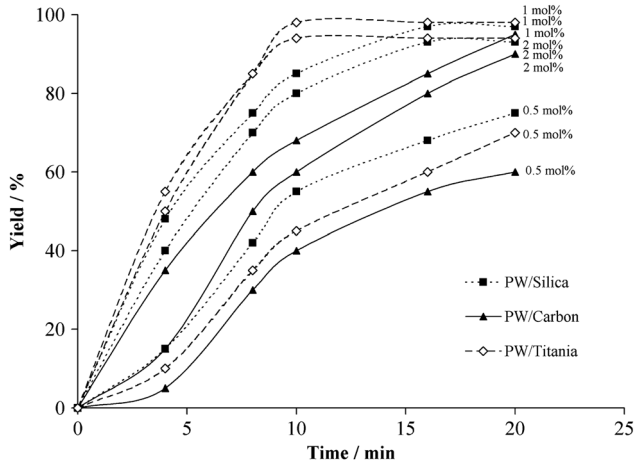



**Figure 1.** Activity pattern of different mole percent of catalysts in model reaction at room temperature and solvent-free condition.

We focus on optimizing the catalyst loading by using the reaction of resorcinol with metylacetoacetate as a model reaction. The activity patterns presented in Figure 1 suggest that 1 mol % of catalyst to resorcinol led to higher result in shorter reaction time. Therefore, we decided to extend the scope of the reaction using only 1 mol % of the catalyst to resorcinol. The reaction was carried using different molar ratios of resorcinol:methylacetoacetate (1:1, 1:1.5, and 1:2) in the presence of $PW/TiO_2$. The yield and reaction time show no significant improvement with increasing the amount of methylacetoacetate. Corresponding product was obtained in 97, 95, and 98% after 11, 10, and 10 min for 1:1, 1:1.5, and 1:2 molar ratios, respectively.

The effect of various solvents was investigated in model reaction of resorcinol with methylacetoacetate using supported (40 wt %) $PW/SiO_2$ (1 mol %). The solvent-free system has some beneficial advantages such as shorter reaction times, lower temperature, higher yields. In addition, in some cases the reaction dose not proceed in solvent system (Table 3) or involve side products..

Afterward, the study was extended to a variety of monohydric and polyhydric phenols, and also the behavior of $PW/SiO_2$, PW/C, and $PW/TiO_2$ as catalysts was studied, which were selected because of the higher activity. For most of substrates, the reactions worked well. Both of the acetoacetic esters (ethyl and methyl) reacted almost similarly to produce coumarin (Tables 4–6, entry 10). However, other phenols having one phenol ring (Tables 4–6, entries 2, 3, 7, and 8) also required a higher temperature of 60°C similar to α-naphthol. It is worth mentioning that the present procedure showed no evidence for the formation of side products of the chromanone type [51]. These results show that besides the catalyst acidity and the reactivity of phenolic substrates, the structural and textural features of catalyst could also play a significant role in influencing the course of this reaction.

The experimental procedure with these catalysts is very simple, and the catalysts can be removed easily by washing and filtration. Hence, there will not be any unnecessary acidic waste streams to create environmentally hazardous pollution. To investigate the reusability of catalysts, $PW/TiO_2$, $PW/SiO_2$, and PW/C in model reaction were rinsed with acetonitrile, filtered off, and dried under ambient conditions for 2 h, after that calcinated at 150°C. As presented in Figure 2, declines were observed in the conversions of resorcinol, from 98 (after 11 min), 98 (after 17 min), and 95 (after 20 min) to 90, 87, and 85% for $PW/TiO_2$, $PW/SiO_2$, and PW/C, respectively when the cycles go from fresh to fourth recycle. Nevertheless, the selectivity to 7-hydroxy-4-methylcoumarin did not change; it remained constant for all four cycles.

## EXPERIMENTAL

PW, SiW, and PMo were used from Aldrich, Merck, and activated carbon, KSF, and K10 montmorillonite were purchased from Fluka. Aerosil silica and titania were obtained from Degussa. γ-Alumina was obtained from Aldrich. $[(n\text{-}C_4H_9)_4N]$ Br, $Cs_2CO_3$, $TiCl_4$, $SnCl_4$, and sodium molybdate from Merck, and $SnCl_2$ and $ZnCl_2$ were used from Fluka. The organic materials were commercially available and purchased from Fluka, Merck, and Aldrich chemical companies.

FTIR spectra were recorded with KBr pellets using a Shimadzu 470 spectrophotometer. $^1$H-NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. Melting points were determined using a digital Gallenkamp apparatus and are uncorrected.

**Preparation of catalysts.** $H_{3+x}PMo_{12-x}V_xO_{40}$, $[(t\text{-}Bu)_4N]_4PW_{11}CoO_{39}$, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalysts were prepared according to our previously published article [44]. The synthesis of $[(n\text{-}Bu)_4N]_5PMo_2W_9(Sn^{2+}\cdot H_2O)O_{39}$, $[(n\text{-}Bu)_4N]_3PMo_2W_9(Sn^{4+}\cdot H_2O)O_{39}$, $[(n\text{-}Bu)_4N]_3PMo_2W_9(Ti^{4+}\cdot H_2O)O_{39}$, and $[(n\text{-}Bu)_4N]_5PMo_2W_9(Zn^{2+}\cdot H_2O)O_{39}$ was started with the preparation of $\alpha\text{-}K_7PMo_2W_9O_{39}\cdot 19H_2O$ from $\beta\text{-}Na_8HPW_9O_{34}\cdot 24H_2O$ and sodium molybdate, according to the procedure described previously [44].

**Table 3**

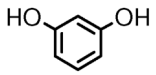
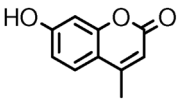
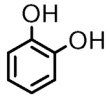
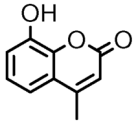
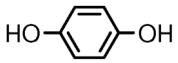
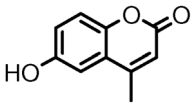
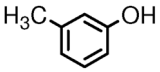
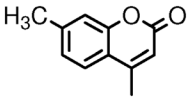
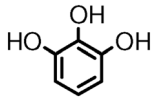
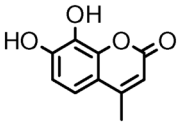
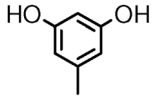
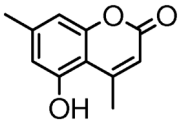
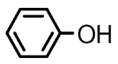
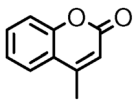
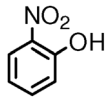
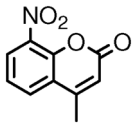
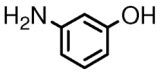
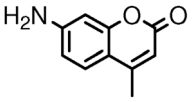
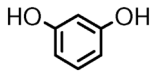
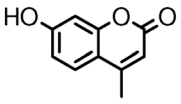
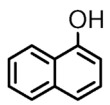
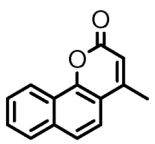
Effect of Various Solvents or Solvent-Less Condition in the Reaction of Methylacetoacetate with Resorcinol.

| Entry | Solvent | Time[a] | Yield (%)[b] |
|---|---|---|---|
| 1 | Acetonitrile | 30 h | No reaction |
| 2 | Dioxane | 30 h | No reaction |
| 3 | Toluene | 30 h (6 h[c]) | No reaction (60) |
| 4 | $H_2O$ | 30 h | No reaction |
| 5 | Methylacetoacetate | 20 min | 13 |
| 6 | Solvent-free | 17 min | 98 |

[a]Reaction proceeds at room temperature.
[b]Isolated yield.
[c]Reaction proceeds at 100°C.

**Table 4**

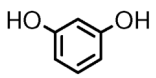
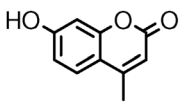
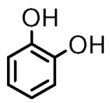
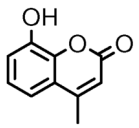
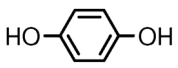
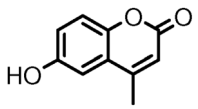
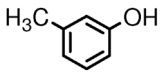
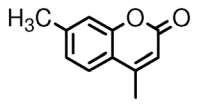
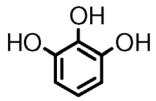
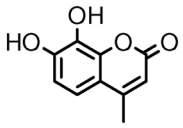
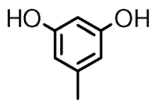
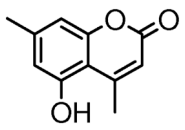
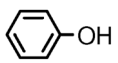
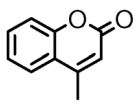
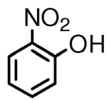
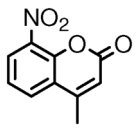
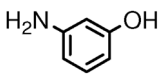
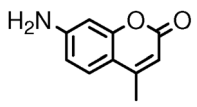
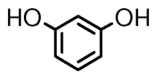
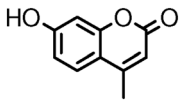
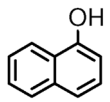
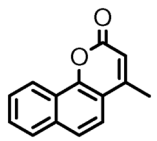
Synthesis of Various Coumarins in the Presence of $PW/SiO_2$.

| Entry | Substrate | Product | *T* (°C) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 |  |  | RT | 17 | 98 |
| 2 |  |  | 60 | 50 | 91 |
| 3 |  |  | 60 | 7 | 82 |
| 4 |  |  | RT | 58 | 85 |
| 5 |  |  | RT | 40 | 96 |
| 6 |  |  | RT | 60 | 84 |
| 7 |  |  | 60 | 5 | 71 |
| 8 |  |  | 60 | 11 | 83 |
| 9 |  |  | RT | 11 | 91 |
| 10[b] |  |  | RT | 25 | 90 |
| 11 |  |  | 60 | 15 | 76 |

[a]Isolated yield.
[b]β-ketoester is ethylacetoacetate.

**Table 5**

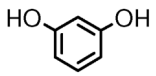
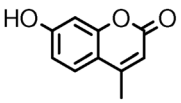
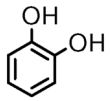
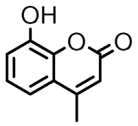
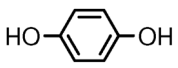
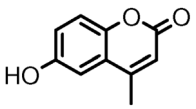
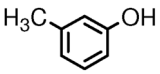
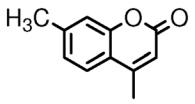
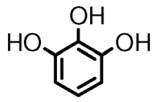
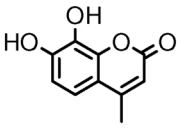
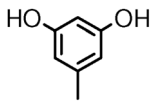
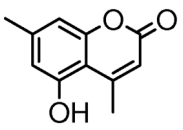
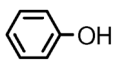
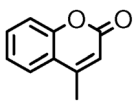
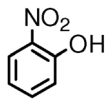
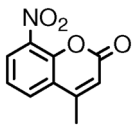
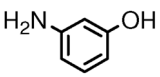
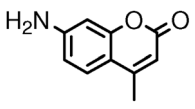
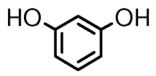
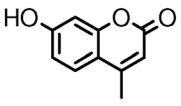
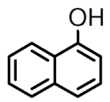
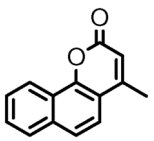
5Synthesis of Various Coumarins in the Presence of $PW/TiO_2$.

| Entry | Substrate | Product | *T* (°C) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 |  |  | RT | 11 | 98 |
| 2 |  |  | 60 | 3 | 98 |
| 3 |  |  | 60 | 5 | 98 |
| 4 |  |  | RT | 45 | 94 |
| 5 |  |  | RT | 35 | 91 |
| 6 |  |  | RT | 65 | 89 |
| 7 |  |  | 60 | 8 | 72 |
| 8 |  |  | 60 | 9 | 96 |
| 9 |  |  | RT | 6 | 95 |
| 10[b] |  |  | RT | 27 | 98 |
| 11 |  |  | 60 | 8 | 90 |

[a]Isolated yield.
[b]β-ketoester is ethylacetoacetate.

**Table 6**

6Synthesis of Various Coumarins in the Presence of PW/C.

| Entry | Substrate | Product | *T* (°C) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 |  |  | RT | 20 | 95 |
| 2 |  |  | 60 | 6 | 71 |
| 3 |  |  | 60 | 10 | 92 |
| 4 |  |  | 60 | 7 | 91 |
| 5 |  |  | RT | 47 | 90 |
| 6 |  |  | RT | 55 | 61 |
| 7 |  |  | 60 | 8 | 49 |
| 8 |  |  | 60 | 12 | 73 |
| 9 |  |  | RT | 13 | 94 |
| 10[b] |  |  | RT | 30 | 95 |
| 11 |  |  | 60 | 12 | 61 |

[a]Isolated yield.
[b]β-ketoester is ethylacetoacetate.

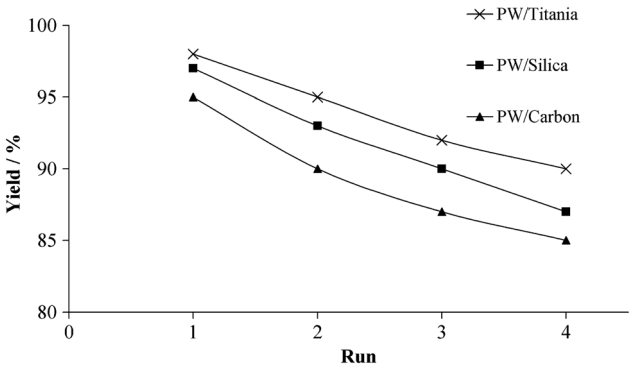



**Figure 2.** Synthesis of 7-hydroxy-4-methyl coumarin with reused catalysts after 17, 11, and 20 min for PW/ SiO2, PW/ TiO2, and PW/C, respectively.

$K_5CoW_{12}O_{40}$ and $K_7PTi_2W_{10}O_{40}$ catalysts were prepared and purified by literature procedures [52], [53].

PW/support catalysts were prepared by impregnation method. The solution of PW was used to impregnate activated carbon, silica, alumina, titania, KSF, and K10 montmorillonite as supports, followed by drying as described in our previously published articles [45], [46].

**General procedure for preparation of coumarins.** The Pechmann reaction was carried out under solvent and solvent-free conditions. (a) solvent: a mixture of methylacetoacetate and resorcinol with molar ratio of 1:1 and solvent (4 mL) was stirred at room temperature in the presence of appropriate amount of the solid catalysts (0.5–2 mol %). Progress of the reaction was monitored by TLC. The catalyst was separated by filtration and washed with $CH_3CN$. The crude of the reaction was washed with a solution of 5% NaOH (3 × 5 mL) and then with water. The organic solution was dried over anhydrous $Na_2SO_4$, filtered, and the solvent was evaporated and subsequently the residue was recrystallized to obtain corresponding coumarins. (b) solvent free: 1 mmol phenolic substrate and 1 mmol β-ketoester were mixed and an appropriate amount of the catalyst (0.5–2 mol %) was added. The reaction mixture was crushed at room temperature or at 60° C. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was extracted with hot toluene (3 × 15 mL). The solvent was evaporated and crude product was recrystallized from a mixture of water and ethanol. All products were identified by comparing of their spectral data with those of the authentic samples [54–59].

**7-Hydroxy-4-methylcoumarin (Table 4, entry 1).** mp 183–184° C; IR: 3086–3012 (C═H), 1676 (C—O), 1063 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.42 (s, 3H, Me), 6.41 (s, 1H, C—CH), 7.76 (m, 1H), 7.83 (q, 1H), 8.01 (m, 1H), OH was not observed.

**8-Hydroxy-4-methylcoumarin (Table 4, entry 2).** mp 168–171°C; IR: 3271–3085 (C═H), 1690 (C—O), 1060 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.41 (s, 3H, Me), 6.23 (s, 1H, C—CH), 6.98 (m, 1H), 7.33 (m, 1H), 7.37 (m, 1H), OH was not observed.

**6-Hydroxy-4-methylcoumarin (Table 4, entry 3).** mp 240–242° C; IR: 3275–3080 (C═H), 1690 (C—O), 1065 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.52 (s, 3H, Me), 6.29 (s, 1H, C—CH), 6.32 (m, 1H), 7.00 (m, 1H), 7.10 (m, 1H), OH was not observed.

**7,4-Dimethylcoumarin (Table 4, entry 4).** mp 134–135°C; IR: 3030–2970 (C═H), 1705 C—O), 1071 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.61 (s, 3H, Me), 2.84 (s, 3H, Me), 6.38 (s, 1H, C—CH), 7.08–7.64 (m, 3H).

**7,8-Dihydroxy-4-methylcoumarin (Table 4, entry 5).** mp 233–235°C; IR: 3235–3101 (C═H), 1650 (C—O), 1061 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.43 (s, 3H, Me), 6.20 (s, 1H, C—CH), 6.93–7.29 (m, 2H), OH was not observed.

**5-Hydroxy-4,7-dimethylcoumarin (Table 4, entry 6).** mp 261–262°C; IR: 3155–3091 (C═H), 1661 (C—O), 1072 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.32 (s, 3H, Me), 2.58 (s, 3H, Me), 6.02 (s, 1H, C—CH), 6.61 (s, 1H), 6.70 (s, 1H), 10.55 (s, 1H, OH).

**4-Methylcoumarin (Table 4, entry 7).** mp 81–83°C; IR: 3110–2998 (C═H), 1666 (C—O), 1058 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.63 (s, 3H, Me), 6.51 (s, 1H, C—CH), 7.28–7.61 (m, 4H).

**8-Nitro-4-methylcoumarin (Table 4, entry 8).** mp 184–185°C; IR: 3011–2981 (C═H), 1625 (C—O), 1052 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.41 (s, 3H, Me), 6.19 (s, 1H, C—CH), 7.37 (m, 1H), 7.73 (m, 1H), 7.94 (m, 1H).

**7-Amino-4-methylcoumarin (Table 4, entry 9).** mp 223–225°C; IR: 3079–2881 (C═H), 1665 (C—O), 10565 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.01 (s, 3H, Me), 4.53 (s, 2H, $NH_2$), 6.33 (s, 1H, C—CH), 6.72 (m, 1H), 7.68 (m, 1H), 7.89 (m, 1H).

**4-Methylnaphtho-(1,2-b)-pyran-2-one (Table 4, entry 11).** mp 151–154°C; IR: 3061–3019 (C═H), 1720 (C—O), 1090 (C═O) $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 2.60 (s, 3H, Me), 6.43 (s, 1H, C—CH), 7.67 (m, 2H), 7.82 (m, 2H), 8.02 (m, 1H), 8.51 (m, 1H).

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