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Single-step synthesis of 4-phenyl and 3,4-dihydro-4-phenyl coumarins using a recyclable Preyssler heteropolyacid catalyst under solvent-free reaction conditions

Angélica M. Escobar[1] · Diego M. Ruiz[2] · Juan C. Autino[2] · Gustavo P. Romanelli[1,2]

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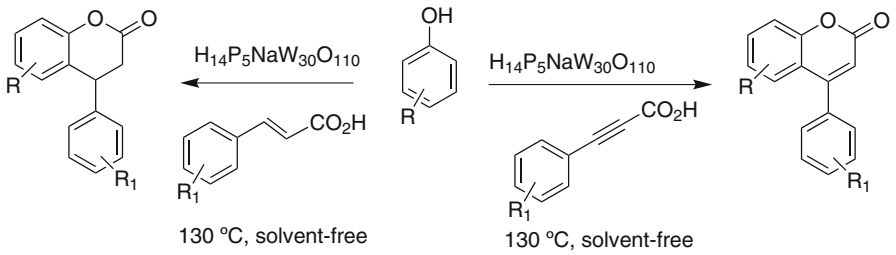
Abstract 4-Phenyl and 3,4-dihydro-4-phenylcoumarins were prepared by direct esterification of phenols with phenylpropiolic and cinnamic acids, respectively, using a compound with Preyssler structure ($H_{14}P_5NaW_{30}O_{110}$) (PA) as heterogeneous catalyst under solvent-free reaction conditions, at 130 °C, in a short reaction time (2 h). Under these conditions, very good yields (11 examples: 61 %–90 %), free of secondary products, were obtained. The catalyst is recyclable, nontoxic, neither air nor moisture sensitive, and easy to handle. The described methodology is a clean and useful alternative to synthesize oxygenated heterocycles based on a coumarin skeleton.
Graphical abstract



Keywords 4-Phenylcoumarins · 4-Phenyl-3 · 4-Dihydrocoumarins · Preyssler catalyst · Recyclable catalyst · Solvent-free reaction conditions

✉ Gustavo P. Romanelli
gpr@quimica.unlp.edu.ar

[1] Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J. J. Ronco" (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, 1900 La Plata, Argentina

[2] CISaV, Cátedra de Química Orgánica, Facultad de Ciencias Agrarias y Forestales, UNLP, Calles 60 y 119, B1904AAN La Plata, Argentina

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Introduction

Heterocyclic compounds bearing coumarins are an important family of substances that play a key role in organic synthesis, since they are present in a variety of naturally occurring compounds. Particularly, both natural and synthetic molecules containing coumarin moiety have interesting pharmacological and biological properties [1].

Specifically, coumarins containing a 4-phenyl group have attracted wide attention due to their interesting and unique properties such as antimalarial [2], anticancer [3], anti-inflammatory [4], and fungicide activity [5]. Besides, some 4-phenylcoumarins also show antiviral activity, for example, mesuol inhibits HIV replication in cells [6] and calocoumarin A acts on the Epstein-Barr virus that causes mononucleosis [7] (Fig. 1a, b).

Furthermore, 3,4-dihydrobenzopyran-2-ones or dihydrocoumarins are well-known as food flavoring [8], are used in perfumery industries [9] and as fragrance in cosmetics [10]. 4-Phenyl-3,4-dihydrocoumarins are natural or synthetic compounds that exhibit some interesting activities such as pesticides [11], antivirals [12], antihypertensives [13], aldose reductase inhibitors [14] and antiherpetic agents [15]. For instance, isorecedensolide and recedensolide (Fig. 1c) showed activity against human cervical epitheloid carcinoma [16].

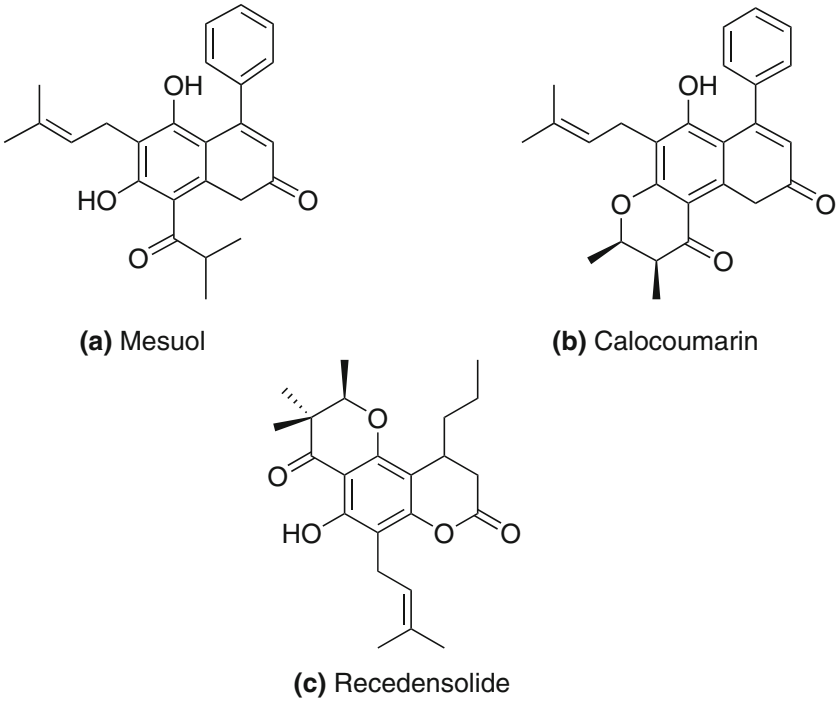


Fig. 1 Bioactive coumarins and dihydrocoumarins

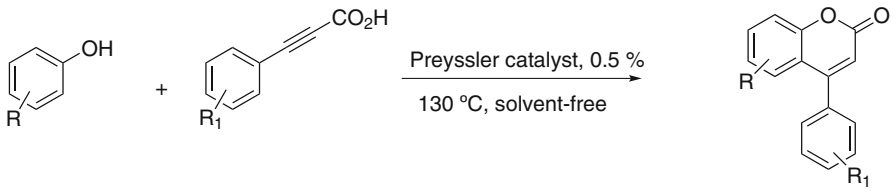
Among the traditional methods for the synthesis of 4-phenylcoumarins are the Pechmann reaction for the condensation of phenols with benzoylacetic acid using acid catalysts such as HCl, P_2O_5, BF_3 $ZnCl_2$, and heteropolyacids (HPA) [17–19]; the Perkin condensation between *o*-hydroxybenzophenones and Ac_2O using AcONa as catalyst [17]; the Wittig reaction of *o*-hydroxybenzophenones using ethoxycarbonyl triphenylphosphorane in benzene [17]; the Houben-Hoesch reaction of benzoylacetonitriles with phenol using $ZnCl_2$/HCl as catalyst, and the arylation of coumarins [17]. Particularly, the Pondorff reaction involves the reaction of phenylpropiolic acid with substituted phenol using an acid catalyst such as TFA [20], P_2O_5/H_3PO_4 [21], montmorillonite K-10 [22] and HPA [23].

The methods for the synthesis of 4-phenyl-3,4-dihydrocoumarins include the catalytic hydrogenation of coumarins [24–26], the Pondorff reaction for the condensation of phenols with α, β-unsaturated acids in the presence of an acid catalyst (for example, H_2SO_4 [17], $P_2O_5/H_3PO_4H_3$ [27], TFA [28], BF_3 [29], zeolites [30], and montmorillonite K-10 using microwave irradiation [22]), arylacrylate lactonization [20, 31–33], Houben-Hoesch condensation of phenols with α,β-unsaturated nitriles in the presence of $ZnCl_2$ [17] or $AlCl_3$/HCl [34], consecutive Friedel–Crafts alkylation-acylation [35], and via Fischer carbenes [36].

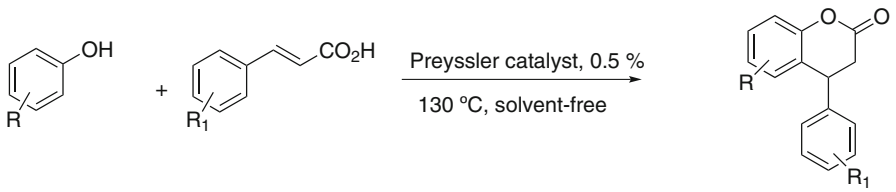
On the other hand, the use of heterogeneous catalysts has been widely studied because they are easy to remove from the reaction media by simple filtration after completion of the reaction and in general, they are reusable without appreciable loss of their catalytic activity [37, 38].

Heteropolyacids (HPA) are well-defined molecular arrangements with remarkable and useful applications. The main property is their reusability and the possibility of generating heterogeneous catalysts [39]. Among the various possible HPA structures, the Keggin-type primary structure deserves to be mentioned due to its widely reported applications [40, 41]. As part of a research project to develop environmentally friendly organic reactions, we used HPA with Preyssler structure, in bulk or silica-supported, as a green and recyclable catalyst, in the protection/deprotection of functional groups [42], and in the synthesis of diverse organic compounds such as esters of cinnamic acids from the reaction between phenols and imidoalcohols [43], *N*-sulfonyl-1,2,3,4-tetrahydroisoquinolines [44], flavones [45], 3*H*-1,5-benzodiazepines [46], and fluorinated hexahydropyrimidines [47].

In the present work we describe the use of a Preyssler heteropolyacid ($H_{14}P_5NaW_{30}O_{110}$) as a recyclable acid catalyst in the synthesis of coumarin



Scheme 1 Synthesis of 4-phenylcoumarins



Scheme 2 Synthesis of 4-phenyl-3,4-dihydrocoumarins

derivatives. Scheme 1 shows the synthesis of 4-phenylcoumarins and Scheme 2 the synthesis of 4-phenyl-3,4-dihydro-4-phenylcoumarins.

Experimental

General

Chemicals were purchased from Aldrich, Fluka and Merck, and were freshly used after purification by standard procedures (distillation and recrystallization). All the reactions were monitored by TLC on precoated silica gel plates (254 mm). Flash column chromatography was performed with 230–400 mesh silica gel. All the yields were calculated from crystallized products. All the products were identified by comparison of physical data (mp, TLC and NMR) with those reported or with those of authentic samples prepared by the respective conventional methods using sulfuric acid as catalyst.

Instrumentation

Melting points of the compounds were determined in sealed capillary tubes and are uncorrected. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker instrument 400 MHz model as $CDCl_3$ solutions, and the chemical shifts were expressed in δ units with Me_4Si (TMS) as the internal standard.

Catalyst preparation

For the preparation of the Preyssler salt $K_{12,5}Na_{1,5}(NaP_5W_{30}O_{110})\cdot 15H_2O$ (PS), a procedure described by Creaser and coworkers [48] was used with minor modifications. In a typical experiment 16.3 g (0.05 mol) $Na_2WO_4.2H_2O$ was dissolved in 15 ml water and mixed at 65 °C for 45 min. The solution was cooled to 20 °C and then, 14 ml concentrated phosphoric acid (85 %) was added. The resulting yellow solution was refluxed for 24 h. The color turned to dark green at the end of reaction. The solution was brought to room temperature, diluted with 20 ml water and then, 10 g potassium chloride was added with stirring. The mixture was stirred for 60 min and then heated up to dryness, and a greenish solid was obtained. This raw product was dissolved in 35 ml warm water and upon cooling to room

temperature white crystals formed, which were collected and recrystallized from boiling water (yield, 21 %). The heteropolyanion was converted to its corresponding acid $H_{14}(NaP_5W_{30}O_{110})$ (PA) by passing an aqueous solution of PS through a Dowex-50 W-×8 ion exchange column.

Catalytic test: 4-phenylcoumarins

The catalyst was dried overnight prior to use. A mixture of the corresponding phenol (1 mmol), phenylpropiolic acid (1 mmol) and PA catalyst (0.5 mmol %) was placed in an open glass tube (20 ml) and stirred at 120 °C for the indicated time. When the reaction time was over, the reaction mixture was extracted with hot toluene (2 × 3 ml). The solution was concentrated in vacuum, and the crude product was recrystallized from methanol or ethanol. Alternatively, the catalyst was extracted with water (3 × 5 ml) and the crude product was recrystallized from methanol or ethanol.

3,4-Dihydro-4-phenylcoumarins

The catalyst was dried overnight prior to use. A mixture of the corresponding phenol (1 mmol), cinnamic acid (1 mmol) and PA catalyst (0.5 mmol %) was placed in an open glass tube (20 ml) and stirred at 130 °C for the indicated time. When the reaction time was over, the reaction mixture was extracted with hot toluene (2 × 3 ml). The extract was washed with H_2O (2 ml) and then dried with anhydrous sodium sulfate and filtered. Evaporation of the solvent under reduced pressure and recrystallization from methanol or ethanol gave the pure products.

Catalyst reuse

Stability tests of the bulk PA catalysts were performed running four consecutive experiments, under the same reaction conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed with toluene (2 × 2 ml), dried under vacuum, and then reused.

Characterization data of compounds

Al spectra correspond to the products achieved at the best reaction conditions (time = 2 h, temperature = 90 °C, catalyst = 0.5 %).

4-Phenylcoumarin (entry 1): mp: 102–104 °C (methanol) (lit. mp: 105 °C [23]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (s, 1H), 7.22 (dd, 2H, J = 2.5, 8 Hz), 7.30 (m, 5H), 7.50 (dd, 2H, J = 2.5, 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.1, 121.4, 125.1, 126.1, 126.3, 126.5, 127.5, 127.8, 128.1, 135.0, 148.1, 159.2, 162.2.

7-Hydroxy-4-phenylcoumarin (entry 2): mp: 238–240 °C (methanol) (lit. mp: 240 °C [23]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (s, 1H), 6.71 (dd, 2H, J = 2.5, 8 Hz), 7.46 (d, 1H, J = 8 Hz), 7.49–7.62 (m, 5H), 7.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.0, 105.7, 112.4, 120.3, 126.0, 127.4, 127.8, 128.1, 135.2, 151.3, 158.6, 158.9, 162.0.

7-Methoxy-4-phenylcoumarin (entry 3): mp: 107–108 °C (methanol) (lit mp: 106–108 °C [49]); ^{1}H NMR (400 MHz, CDCl3) δ 7.54−7.47 (m, 3H), 7.48 − 7.42 (m, 2H), 7.39 (d, J = 8.9 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 6.77 (dd, J = 8.9, 2.5 Hz, 1H), 6.21 (s, 1H), 3.88 (s, 3H); 13C NMR (100 MHz, CDCl3) δ163.8, 161.2, 156.0, 155.7, 135.6, 129.5, 128.9, 128.4, 128.2, 112.5,112.3, 111.9, 101.4, 54.9.

6-Methyl-4-phenylcoumarin (entry 4): mp: 135–137 (methanol) (lit. mp: 134.7–135.1 °C [50]) ^{1}H NMR (300 MHz, CDCl3) δ 2.35 (s, 3H, CH3), 6.34 (s, 1H, vinyl), 7.27 (s,1H, aryl), 7.32 (d, *J*) 8.1 Hz, 1H, aryl), 7.38 (dd, *J*) 2.1, 8.1 Hz, 1H, aryl), 7.45 (m, 2H, aryl), 7.55 (m, 3H, aryl); 13C NMR (100 MHz, CDCl3) δ 20.9, 115.1, 117.0, 118.6, 126.8,128.4, 128.8, 129.5, 132.8, 133.8, 135.34, 152.3, 155.5,160.9.

6-Methoxy-4-phenylcoumarin (entry 5): mp 147–149 °C (methanol) (lit. mp: 148–149 °C [49]) ^{1}H NMR (400 MHz, CDCl3) δ 7.57 − 7.50 (m, 3H), 7.46 (dd, J = 6.6, 2.9 Hz, 2H), 7.34 (d, J = 9.0 Hz, 1H), 7.13 (dd, *J*= 9.0, 2.9 Hz, 1H), 6.93 (d, J = 2.9 Hz, 1H), 6.38 (s, 1H), 3.74 (s, 3H); 13C NMR CDCl3) δ 161.1, 156.0, 155.5, 148.7, 135.4, 129.7, 129.1, 128.5, 119.6, 119.1, 118.4, 115.8, 110.1, 55.9.

4-(4-Methoxyphenyl)-coumarin (entry 6): mp: 128–129 °C (methanol) (lit mp: 129–130 °C [51]) ^{1}H NMR (400 MHz, CDCl3) δ 3.91 (s, 3H), 6.35 (s, 1H), 7.05 (d J 8.8 Hz, 2H), 7.24 (dd, J 8.5, 7.2, 1,2 Hz, 1H), 7.39–7.42 (d, J 8.7 Hz, 2 H), 7.54 (dd, *J* 7.8, 1.5 Hz), 1H), 7.57 (d, *J* 7.8 Hz, 1H) Carbon: 55.5, 114.1, 114.5, 117.5,119.2, 124.0, 127.0, 127.7,129.9, 131.8, 154.2, 155.3, 159.9

4-Phenyl-3,4-dihydrocoumarin (entry 7): mp: 78–79 °C (methanol) (lit. mp: 80–82 °C [23]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (dd, 2H, J = 6, 16 Hz), 4.37 (t, 1H, J = 6 Hz), 6.99 (d, 1H, J = 8 Hz), 7.01 (d, 1H, J = 8 Hz), 7.08–7.14 (m, 1H), 7.26–7.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.1, 40.7, 125.3, 125.5, 125.8, 126.8, 127.5, 129.8, 130.4, 143.3, 148.6, 167.7.

6-Methyl-4-phenyl-3,4-dihydrocoumarin (entry 8): mp: 80–81 °C (methanol) (lit. mp: 80–83 °C [52]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.98–3.10 (m, 2H), 4.32 (t, 1H, J = 6.8 Hz), 6.82 (s, 1H), 7.05 (d, 1H, J = 8 Hz), 7.15 (d, 1 H, J = 8 Hz), 7.28 (d, 2H, J = 5.1 Hz), 7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 36.3, 40.2, 125.4, 125.7, 125.8, 127.0, 128.1, 129.9, 135.5, 143.3, 148.5, 17.7

7-Methyl-4-phenyl-3,4-dihydrocoumarin (entry 9): mp 124–125 °C (methanol) (lit. mp: 124 °C [52]); 1H NMR (400 MHz, CDCl3) δ 2.38 (s, 3H), δ 3.13–2.99 (m, 2H), δ 4.35(t, 1H, J = 6.80 Hz), δ 6.92(q, 2H, J = 8 Hz), δ 6.98 (s, 1H), δ 7.18 (d, 2H, J = 7.6 Hz), δ 7.35(m, 3H). 13C NMR (100 MHz, CDCl3) δ 21.5, 37.2, 40.8, 125.4, 125.7, 125.8, 127.5, 129.8, 131.4, 135.5 143.3, 148.6, 167.7.

8-Methyl-4-phenyl-3,4-dihydrocoumarin (entry 10): mp 105–107 (methanol) (lit. mp: 106–108 °C [52]); ^{1}H NMR (400 MHz, CDCl3) δ 2.36 (s,3H), δ 3.10–2.99 (m, 2H), δ 4.32 (t, 1H, J = 6.8 Hz), δ 6.81 (d, 1H, J = 7.6 Hz), δ 6.98 (t, 1H, J = 7.6 Hz), δ 7.15 (d, 3H, J = 7.2 Hz), δ 7.33–7.26 (m, 3H).13C NMR (100 MHz, CDCl3) δ 21.4, 37.3, 40.9, 125.3, 125.7, 125.8, 129.8, 131.4, 135.5, 135.7, 143.3, 148.6, 167.7.

4(4-Methylphenyl-3,4-dihydrocoumarin (entry 11): mp 103–104 °C (methanol) mp: 103–104 °C (lit. no data); ^{1}H-RMN (400 MHz, $CDCl_3$), δ (ppm): 1,25 (3H, s); 3.10–3.16 (2H, dd, J = 6 Hz; 16 Hz); 4.37 (1H, t, J = 6 Hz); 6.99 (1H, d,

$J = 8$ Hz); 7.01 (1H, d, $J = 8$ Hz); 7.08–7.14 (1H, m, $J = 8$ Hz); 7.15–7.21 (2H, m, $J = 8$ Hz); 7.27–7.39 (4H, m). ^{13}C-RMN (100 MHz, $CDCl_3$): 19.8; 37.2; 40.7; 125.0; 125.5; 125.8; 126.7; 127.5; 128.3; 129.7; 133.6; 140.2; 148.2; 167.5.

Green metrics

In order to quantify how much 'greener' the presented methodology is, various green metric parameters were calculated for each reaction performed, namely, quantitative factors such as atom economy (AE), atomic efficiency factor (E), process mass intensity (PMI) and semiquantitative EcoScale.

Results and discussion

Optimal reaction conditions were examined employing phenol and phenylpropiolic acid as test reaction substrate under solvent-free reaction conditions at 130 °C for 2 h. Without the presence of catalyst, no reaction was observed. First, the influence of the reaction temperature on 4-phenylcoumarin synthesis was tested using PA. The tested experimental reaction conditions were: phenol (1 mmol), phenylpropiolic acid (1 mmol) catalyst (0.005 mmol), and 2 h of reaction time under solvent-free reaction conditions. The results are listed in Table 1. In order to obtain the optimal temperature, four temperatures (90, 110, 130 and 150 °C, Table 1) were tested. No reaction was observed at 90 °C (entry 1, Table 1).

A temperature increase leads to a higher 4-phenylcoumarin yield. For example, the yield of 4-phenylcoumarin for a reaction time of 2 h at 110 °C was only 54 % (entry 2, Table 1), whereas at 130 °C the yield was 90 % (entry 3, Table 1). Finally, at 150 °C the reaction yield was lower, 62 %, (entry 4, Table 1) due to the several unidentified side products that were detected by thin layer chromatography.

For this reason, 130 °C was employed as the ideal temperature to continue with the next experiment for the analysis of the other reaction variables. Table 2 shows the results for 4-phenylcoumarin synthesis at different reaction times using PA catalyst at 130 °C. The experimental reaction conditions were: phenol (1 mmol), phenylpropiolic acid (1 mmol), catalyst (0.005 mmol), at 130 °C under solvent-free

Table 1 Effect of temperature on 4-phenylcoumarin yields (%)

Entry	Temperature (°C)	Yield[a] (%)
1	90	–
2	110	54
3	130	90
4	150	62

Reaction conditions: phenol, 1 mmol; 3-phenylpropiolic acid, 1 mmol; catalyst, 0.5 % mmol; 2 h; stirring; under solvent-free reaction conditions

[a] Isolated yields

Table 2 Effect of reaction time on 4-phenylcoumarin yields (%)

Entry	Reaction time (h)	Yield[a] (%)
1	0.5	29
2	1	54
3	2	90
4	3	88

Reaction conditions: phenol, 1 mmol; 3-phenylpropiolic acid, 1 mmol; catalyst, 0.5 % mmol; 130 °C; stirring; under solvent-free reaction conditions

[a] Isolated yields

Table 3 Effect of the amount of catalyst on 4-phenylcoumarin yields (%)

Entry	Amount of catalyst (%)	Yield[a] (%)
1	0.1	39
2	0.5	90
3	1	90
4	2	91

Reaction conditions: phenol, 1 mmol; 3-phenylpropiolic acid, 1 mmol; 130 °C; 2 h; stirring; solvent-free reaction conditions

[a] Isolated yields

Table 4 Effect of catalyst reuse on 4-phenylcoumarin yields (%)

Entry	Catalytic cycle	Yield[a] (%)
1	1	90
2	2	88
3	3	84
4	4	80

Reaction conditions: phenol, 1 mmol; 3-phenylpropiolic acid, 1 mmol; catalyst, 0.5 % mmol; 2 h; 130 °C; stirring; in solvent-free reaction conditions

[a] Isolated yields

reaction conditions. It can be observed that the yields of 4-phenylcoumarin increased with the reaction time up to 2 h and then remained practically constant (ca. 90 %, Table 2, entries 3 and 4).

Table 3 shows the effect of the amount of catalyst (PA) on the yield of 4-phenylcoumarin in the reaction. The experimental conditions were: phenol (1 mmol), phenylpropiolic acid (1 mmol), with a reaction time of 2 h at 130 °C under solvent-free reaction conditions, with a variable amount of PA catalyst (0.1, 0.5, 1, and 2 %). It can be seen that the yields increased from 39 to 90 % when the amount of PA increased from 0.1 to 0.5 % (Table 3, entries 1 and 2), and no relevant changes in the reaction yield were observed with further increase in the

Table 5 Synthesis of 4-phenylcoumarins and 4-phenyl-3,4-dihydrocoumarins

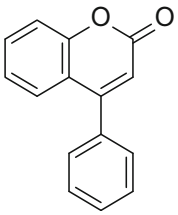
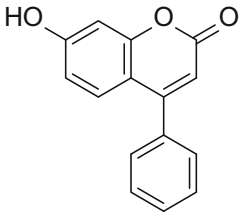
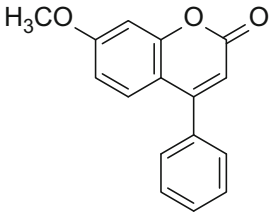
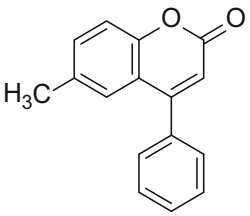
Entry	Product	Yield (%)	AE (%)	E	PMI	EcoScale
1		90	92.5	42.1	43.4	86
2		88	92.9	40.2	41.5	85
3		84	93.3	39.8	40.5	83
4		83	92.9	43.0	44.4	83.5

Table 5 continued

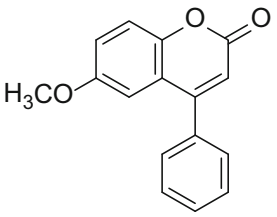
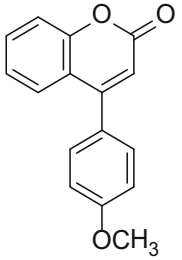
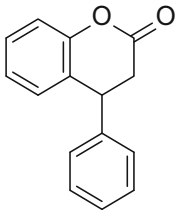
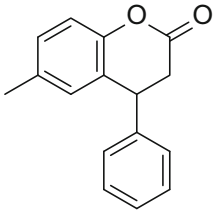
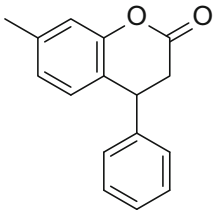
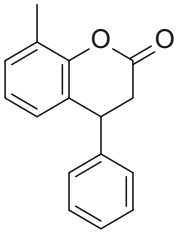
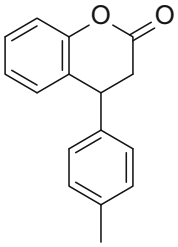
Entry	Product	Yield (%)	AE (%)	E	PMI	EcoScale
5		80	93.3	41.7	43.1	81
6		78	93.3	42.8	44.3	80
7		61	92.6	76.4	78.3	56.5
8		77	93.0	56.9	58.5	64.5

Table 5 continued

Entry	Product	Yield (%)	AE (%)	E	PMI	EcoScale
9		73	93.0	60.1	61.7	62.5
10		71	93.0	61.7	63.4	61.5
11		66	93.0	66.4	68.3	59

Reaction conditions: phenols, 1 mmol; 3-phenylpropiolic acid, or cinnamic acid, 1 mmol; catalyst, 0.5 % mmol; 2 h; 130 °C; stirring; in solvent-free conditions

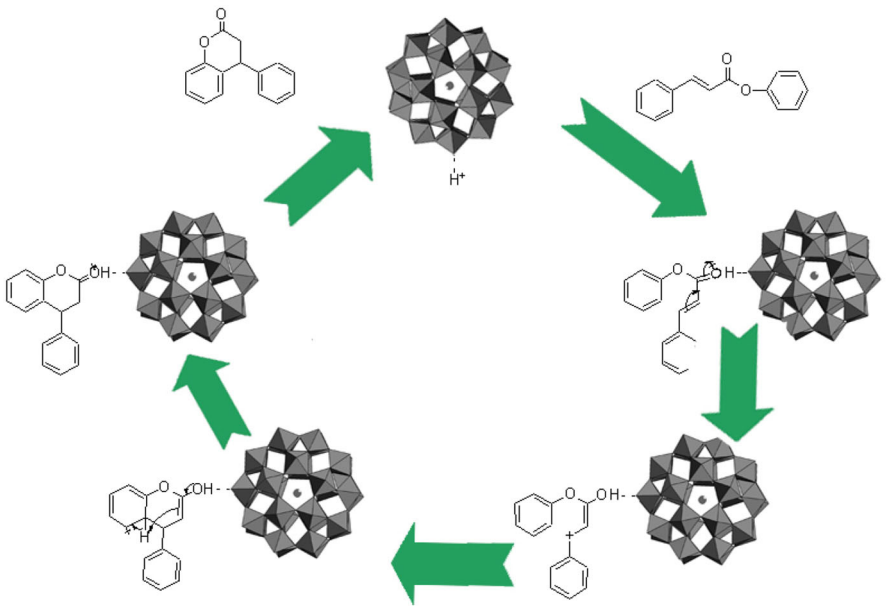
[a] Isolated yields

amount of PA (2 %), (91 %, Table 3, entry 4). Thus, 0.5 % of PA is a suitable amount for performing this reaction.

The reuse of the catalyst was investigated in the consecutive reaction of phenol and phenylpropiolic acid in solvent-free reaction conditions. At the end of each run the catalyst was removed, washed with toluene, dried in vacuum at 25 °C and reused. The results are summarized in Table 4. The catalyst was reused three runs and no appreciable loss of its catalytic activity was observed. The performance of the reactions under the same conditions using PA as catalyst showed 90, 88 and

Table 6 Green metric comparison of classic synthesis methods with the techniques described in this work

Method	Yield (%)	AE (%)	E factor	PMI	EcoScale
Pechmann (coumarins) [17]	39	79.4	98.5	99	28
This paper (coumarins)	90	92.5	42.1	43.4	86
Pondorff (dihydrocoumarins) [30]	70	92.6	109.1	111.1	42
This paper (dihydrocoumarins)	61	92.6	76.4	78.3	56.5



Scheme 3 Proposed mechanism for 3,4-dihydro-4-phenylcoumarin synthesis

84 % of 4-phenylcoumarin yield, respectively. In the four cycles, the reaction yield was 80 % in 3 h.

Using the optimized conditions: phenol (1 mmol), phenylpropiolic acid (1 mmol), PA catalyst (0.5 % mmol) at 130 °C, 2 h of reaction time, and solvent-free conditions (Scheme 1), six substituted 4-phenylcoumarins were prepared (Table 5). In all the experiments, the desired products were obtained with high selectivity.

Similarly, we achieved the sustainable, solvent-free preparation of seven substituted 4-phenyl-3,4-dihydrocoumarins from phenols and α, β-unsaturated carboxylic acids (Scheme 2) using PA as catalyst in the optimized conditions. For example, 6-methyl-4-phenyl-3,4-dihydrocoumarin was obtained in a yield of 77 % and free of secondary products from the reaction of a stoichiometric amount of 4-methylphenol and cinnamic acid, 0.5 % of PA (Table 5, entry 8).

In order to quantify how much 'greener' the methodology is, the atom economy, atomic efficiency factor, process mass intensity, and EcoScale were calculated for each reaction product and the results are also presented in Table 5. The resulting parameters were also compared with classic methods for the synthesis of coumarins and dihydrocoumarins [17, 30]. The results (listed in Table 6) indicate an improvement in the synthesis of coumarins from a green chemistry viewpoint, with better yield, atom economy, environmental factor, process mass intensity and EcoScale factors. Similarly, dihydrocoumarin preparation results in a greener procedure in view of the E-factor, PMI and EcoScale parameters.

Scheme 3 displays a plausible reaction mechanism for 3,4-dihydrophenylcoumarin formation using phenol and cinnamic acid as substrate catalyzed by the Preyssler heteropolyacid (PA).

Conclusions

The procedure described for the synthesis of 4-phenylcoumarins and 3,4-dihydro-4-phenylcoumarins (dihydrocoumarins), using a heteropolyacid with Preyssler primary structure in bulk form, is a clean and useful alternative. The advantages of this methodology are operative simplicity, use of a reusable and noncorrosive solid acid catalyst, soft reaction conditions, low reaction times, and good yields. In these conditions, proved to be greener by various green metric parameters, very good yields (11 examples: 61–90 %) of 4-phenylcoumarin derivatives free of secondary products were obtained.

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