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Silica-bonded *n*-propyldiethylenetriamine sulfamic acid as a recyclable solid acid catalyst for the synthesis of coumarin and biscoumarin derivatives

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ABSTRACT

Silica-bonded *n*-propyldiethylenetriamine sulfamic acid (SBPDSA) was found as an efficient solid acid for the synthesis of coumarins. Coumarin derivatives were obtained *via* the Pechmann condensation reaction of phenols and *β*-keto-esters at 80 °C under solvent-free conditions. Also, biscoumarins were obtained *via* the condensation of aldehydes and 4-hydroxycoumarin in water at reflux conditions. The heterogeneous solid acid showed much the same efficiency when used in consecutive reaction runs.

***Keywords**: Silica-bonded n-propyldiethylenetriamine sulfamic acid, Coumarins, Pechmann reaction, Aromatic aldehydes, Biscoumarins, Solid acids, Catalyst.*

1. Introduction

Coumarins and their derivatives are very important structural motifs that occur widely in natural products [1]. Their synthesis has attracted considerable attention from organic and medicinal chemists for many years as members of this family have wide applications in medicinal chemistry [2], being known as anticancer [3], antioxidants [4], anti-HIV [5], enzymatic inhibitors [6], or vasorelaxants [7]. Besides the medicinal applications, coumarins have been used in fluorescent probes [8], triplet sensitizers [9], and cosmetic industries [10].

Synthetic routes to coumarins include Pechmann condensation, Perkin, Knoevenagel and Reformatsky reactions and by flash vacuum pyrolysis [11-13]. Pechmann condensation has been the most widely applied method for coumarin synthesis, since it proceeds from simple starting materials (phenol and *β*-keto ester) and gives good yields of coumarins with substitution in either pyrone or benzene ring or in both. However, Pechmann condensation utilizes various catalysts, such as sulfuric acid, trifluoroacetic acid, phosphorous pentoxide, $ZrCl_4$, $TiCl_4$, $BiCl_3$, sulphamic acid, scandium (III) triflate, and ionic liquids, which require long reaction times, corrodes reactor, creates by-products and salt waste due to acid neutralization [14-18].

Recently, a number of heterogeneous catalysts such as zeolite H-BETA, Amberlyst 15 [19], sulfated zirconia [20], silica sulfuric acid [21], alum [22], water-tolerant sulfonic acid nanoreactor [23], silica-bonded *S*-sulfonic acid [24], mesoporous zirconium phosphate [25], and ZrPW (zirconium(IV) phosphotungstate) [26], have been employed for this purpose in the Pechmann condensation.

Application of solid acids in organic transformation has important role, because they have many advantages such as easy of handling, decreased reactor and plant corrosion problems and more environmentally safe disposal [23,27-36]. Recently, we prepared a series of silica functionalized *n*-propylsulfamic acids such as silica-bonded *n*-propyldiethylenetriamine sulfamic acid (SBPDSA) and silica-bonded *n*-propylpiperazine sulfamic acid (SBPPSA) and used them as a catalyst for the synthesis of heterocyclic compounds [27-30] (Scheme 1).

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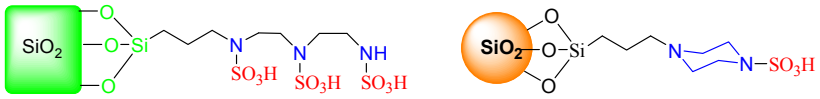


(SBPDSA) (SBPPSA)

Scheme 1. The proposed structure for SBPDSA and SBPPSA.

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All the products were characterized by comparison of their IR, ^{1}HNMR and ^{13}CNMR spectroscopic data and their melting points with the reported values [11-25,37-43]. Silica-bonded *n*-propyldiethylenetriamine sulfamic acid (SBPDSA) [27,28] and silica-bonded *n*-propylpiperazine sulfamic acid (SBPPSA) [29,30] were prepared according to our previous reported procedures.

2.2. General procedure for the synthesis of coumarins

To a mixture of phenolic substrate (1 mmol) and *β*-keto-ester (1 mmol), SBPDSA (0.05 g, 4.9 mol%) was added and magnetically stirred at 80 ˚C under solvent-free conditions. The progress of the reaction was followed by TLC. After completion of the reaction, warm ethanol (2×10 mL) was added and filtered. Ethanol was evaporated under reduced pressure and crude product was recrystallized from hot ethanol. The recovered catalyst was dried and reused for subsequent runs.

2.3. General procedure for the synthesis of biscoumarins

To a mixture of 4-hydroxycoumarin (2 mmol) and aromatic aldehyde (1 mmol) in water (10 mL) catalyst SBPDSA (0.06 g, 5.88 mol%) was added and the mixture was refluxed. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered. The remaining was washed with warm ethanol (3×30 mL) in order to separate heterogeneous catalyst. After cooling the crude products were precipitated. The crude products were purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for subsequent runs.

Selected spectral data

5,7-Dihydroxy-4-methyl-chromen-2-one ***(3a)***:

m.p.= 284-286 ˚C (Lit. [15]: m.p.=283-285 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.44 (s, 3H), 5.67 (d, 1H, *J*= 1.1 Hz), 6.17 (d, 1H, *J*= 2.3 Hz), 6.19 (d, 1H, *J*= 2.3 Hz), 9.48 (s, 1H, OH), 9.59 (s, 1H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 24.3, 95.6, 100.0, 103.4, 109.5, 156.1, 157.1, 158.3, 161.4, 162.2 ppm.

3-Chloro-5,7-dihydroxy-4-methyl-chromen-2-one ***(3b)***:

m.p.= 297-299 ˚C (Lit. [20]: m.p.= 317-319 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.69 (s, 3H), 6.18 (d, 1H, *J* = 2.5 Hz), 6.31 (d, 1H, *J* = 2.5 Hz), 10.36 (s, 1H, OH), 10.69 (s, 1H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 20.2, 95.3, 100.6, 102.7, 114.5, 151.1, 155.0, 157.2, 158.52, 162.0 ppm.

1,3-Dihydroxy-7,8,9,10-tetrahydro-benzo[c]chromen-6-one ***(3c)***:

m.p.= 260-262 ˚C (Lit. [16]: m.p.= 265-266 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 1.64-1.72 (m, 4H), 2.44-2.48 (m, 2H), 3.07-3.12 (m, 2H), 6.29 (s, 2H), 10.30 (brs, 2H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 21.7, 22.6, 24.7, 30.0, 95.5, 100.2, 103.5, 117.2, 151.4, 155.3, 157.6, 159.9, 162.9 ppm.

5,7-Dihydroxy-4-propyl-chromen-2-one ***(3d)***:

m.p.= 234-236 ˚C (Lit. [17]: m.p.= 238 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 0.90 (t, 3H, *J* = 7.3 Hz), 1.52-1.56 (m, 2H), 2.80 (t, 2H, *J* = 7.5 Hz), 5.78 (s, 1H), 6.13 (d, 1H, *J* = 2.4 Hz), 6.22 (d, 1H, *J* = 2.4 Hz), 10.24 (brs, 1H, OH), 10.53 (brs, 1H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 14.7, 23.4, 38.1, 95.6, 100.1, 102.2, 109.2, 157.7, 158.3, 159.4, 161.1, 161.8 ppm.

7-Hydroxy-4-methyl-chromen-2-one ***3e***:

m.p.= 185-187 ˚C (Lit. [15]: m.p.= 184-186 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.29 (s, 3H), 5.96 (s, 1H), 6.71-6.74 (m, 2H), 7.34 (d, 1H, *J*= 8.4 Hz), 9.74 (s, 1H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 19.0, 103.4, 111.2, 112.9, 113.5, 126.0, 153.4, 155.6, 161.7, 162.0 ppm.

7-Hydroxy-4,5-dimethyl-chromen-2-one ***(3f)***:

m.p.= 256-258 ˚C, (Lit. [16]: m.p.= 250-252 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.08 (s, 3H), 2.38 (s, 3H), 5.72 (s, 1H), 6.34 (s, 2H), 9.56 (s, 1H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 21.8, 24.3, 107.4, 108.5, 112.3, 112.4, 143.1, 155.4, 155.5, 156.8, 161.4 ppm.

3-Chloro-7-hydroxy-4,5-dimethyl-chromen-2-one ***3g***:

m.p.= 287-289 ˚C (Lit. [11]: m.p.= 295 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.12 (s, 3H), 2.62 (s, 3H), 6.40 (d, 1H, *J* = 0.75 Hz), 6.43 (d, 1H, *J* = 0.75 Hz), 9.76 (brs, 1H, OH) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 20.7, 21.8, 107.2, 108.4, 113.2, 117.8, 143.2, 150.8, 153.0, 156.5, 157.6.

*3-Hydroxy-1-methyl-7,8,9,10-tetrahydro-benzo[c]-chromen-6-one (**3h**)*:

m.p.= 247-249 ˚C (Lit. [16]: m.p.= 252-253 ˚C). ^{1}HNMR (500 MHz, DMSO-d_6): δ= 1.58-1.68 (m, 4H), 2.24 (s, 3H), 2.33-2.38 (m, 2H), 3.03-3.08 (m, 2H), 6.53 (s, 1H), 6.55 (s, 1H), 10.30 (s, 1H, OH) ppm. ^{13}CNMR (125 MHz, DMSO-d_6): δ= 21.6, 21.8, 22.5, 25.0, 30.1, 107.4, 108.4, 112.9, 120.1, 141.7, 150.3, 153.9, 156.7, 161.4 ppm.

*7,8-Dihydroxy-4-methyl-chromen-2-one (**3i**)*:

m.p.= 240-242 ˚C (Lit. [20]: m.p.= 242-244 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.20 (s, 3H), 5.88 (s, 1H), 6.67 (d, 1H, *J* = 8.6 Hz), 6.84 (d, 1H, *J* = 8.6 Hz), 8.63 (brs, 2H) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 19.1, 111.1, 112.6, 113.6, 115.7, 132.4, 143.6, 149.4, 154.0, 161.4 ppm.

*7-Methoxy-4-methyl-chromen-2-one (**3j**)*:

m.p.= 155-157 ˚C (Lit. [15]: m.p.= 156-158 ˚C). ^{1}HNMR (500 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 2.44 (s, 3H), 3.91 (s, 3H), 6.18 (s, 1H), 6.86 (d, 1H, *J* = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.5 Hz), 7.54 (d, 1H, *J* = 8.8 Hz) ppm. ^{13}CNMR (125 MHz, $CDCl_3$-DMSO-d_6 (2%)): δ= 19.08, 56.16, 101.29, 112.41, 112.71, 114.02, 125.93, 152.93, 155.76, 161.69, 163.09 ppm.

*3,3'-(Phenylmethylene)-bis-(4-hydroxycoumarin) (**4a**)*:

m.p.= 233-234 ˚C (Lit. [37]: m.p.= 230-232 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 6.13 (s, 1H), 7.24-7.50 (m, 9H), 7.64-7.68 (m, 2H), 8.02-8.14 (m, 2H), 11.35 (s, 1H, OH), 11.57 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 36.2, 103.9, 105.7, 116.5, 124.4, 124.9, 126.5, 126.9, 128.7, 132.9, 135.2, 152.3, 152.6, 164.6, 165.8, 166.9 ppm.

*3,3'-(4-Chlorophenylmethylene)-bis-(4-hydroxycoumarin) (**4b**)*:

m.p.= 258-259 ˚C (Lit. [38]: m.p.= 257-259 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 6.07 (s, 1H), 7.18 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.8 Hz), 7.39-7.45 (m, 4H), 7.64-7.69 (m, 2H), 8.02 (d, 1H, *J* = 8.0 Hz), 8.10 (d, 1H, *J* = 7.8 Hz), 11.35 (s, 1H, OH), 11.57 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 35.8, 103.7, 105.3, 116.4, 132.7, 133.1, 133.9, 152.3, 152.6, 164.7, 166.1, 166.9, 169.2 ppm.

*3,3'-(4-Bromophenylmethylene)-bis-(4-hydroxycoumarin) (**4c**)*:

m.p.= 269-270 ˚C (Lit. [39]: m.p.= 266-268 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 6.04 (s, 1H), 7.12 (d, 2H, *J* = 8.4 Hz), 7.39-7.47 (m, 6H), 7.65-7.69 (m, 2H), 8.01-8.10 (m, 2H), 11.35 (s, 1H, OH), 11.56 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 35.9, 103.7, 105.2, 116.4, 116.7, 116.8, 120.8, 124.4, 125.0, 128.4, 131.7, 133.1, 134.5, 152.3, 152.6, 164.7, 166.1, 166.9, 169.2 ppm.

*3,3'-(4-Fluorophenylmethylene)-bis-(4-hydroxycoumarin) (**4d**)*:

m.p.= 220-222 ˚C (Lit. [37]: m.p.= 213-215 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 6.07 (s, 1H), 7.03 (t, 2H, *J* = 8.4 Hz), 7.19-7.23 (m, 2H), 7.42-7.44 (m, 4H), 7.64-7.68 (m, 2H), 8.01-8.10 (m, 2H), 11.35 (s, 1H, OH), 11.57 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 35.7, 104.0, 105.5, 115.4, 115.6, 116.4, 116.7, 116.9, 124.4, 125.0, 128.1, 128.2, 130.8, 130.9, 133.0, 152.3, 152.5, 161.7 (d, $J_{C\text{-}F}$ = 244.0 Hz), 164.6, 165.9, 166.9, 169.2 ppm.

*3,3'-(3-Nitrophenylmethylene)-bis-(4-hydroxycoumarin) (**4e**)*:

m.p.= 213-215 ˚C, (Lit. [40]: m.p.= 212-215 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 6.15 (s, 1H), 7.41-7.48 (m, 4H), 7.54 (t, 1H, *J* = 7.8 Hz), 7.61 (d, 1H, *J* = 7.6 Hz), 7.70 (t, 2H, *J* = 7.8 Hz), 8.02 (d, 1H, *J* = 8.0 Hz), 8.10-8.13 (m, 2H), 8.17 (d, 1H, *J* = 8.0 Hz), 11.41 (s, 1H, OH), 11.60 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 36.2, 103.2, 104.6, 116.3, 116.8, 116.9, 121.8, 122.2, 124.5, 125.2, 125.2, 129.6, 132.8, 133.4, 138.0, 148.8, 152.4, 152.6, 164.9, 166.6, 167.0, 169.2 ppm.

*3,3'-(4-Nitrophenylmethylene)-bis-(4-hydroxycoumarin) (**4f**)*:

m.p.= 237-238 ˚C, (Lit. [41]: m.p.= 232-234 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 6.12 (s, 1H), 7.41-7.46 (m, 6H), 7.68 (t, 2H, *J* = 7.6 Hz), 8.01 (d, 1H, *J* = 7.6 Hz), 8.10 (d, 1H, *J* = 7.6 Hz), 8.20 (d, 2H, *J* = 8.4 Hz), 11.39 (s, 1H, OH), 11.58 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 36.5, 103.3, 104.8, 116.2, 116.7, 116.8, 116.8, 123.9, 124.5, 124.5, 125.2, 125.2, 127.6, 133.4, 143.4, 146.9, 152.3, 152.6, 164.8, 166.4, 167.0, 169.1 ppm.

*3,3'-(p-Tolylmethylene)-bis-(4-hydroxycoumarin) (**4g**)*:

m.p.= 270-271 ˚C (Lit. [42]: m.p.= 269-270 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 2.36 (s, 3H), 6.09 (s, 1H), 7.11-7.17 (m, 4H), 7.44 (d, 4H, *J* = 8.4 Hz), 7.63-7.67 (m, 2H), 8.02-8.09 (m, 2H), 11.33 (s, 1H, OH), 11.55 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 21.0, 35.9, 104.1, 105.8, 117.0, 124.4, 124.9, 129.4, 132.1, 132.8, 136.5, 152.3, 152.5, 164.7, 166.7, 166.9, 169.3 ppm.

*3,3'-(4-Methoxyophenylmethylene)-bis-(4-hydroxycoumarin) (**4h**)*:

m.p.= 253-254 ˚C, (Lit. [42]: m.p.= 249-250 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 3.82 (s, 3H), 6.07 (s, 1H), 6.87 (d, 2H, *J* = 8.4 Hz), 7.14 (d, 2H, *J* = 8.4 Hz), 7.42-7.44 (m, 4H), 7.65 (t, 2H, *J* = 7.6 Hz), 8.03-8.08 (m, 2H), 11.33 (brs, 1H, OH), 11.54 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 35.5, 55.3, 104.2, 105.8, 114.0, 116.6, 117.0, 124.4, 124.9, 127.0, 127.6, 132.8, 152.3, 152.5, 158.4, 164.5, 165.7, 166.8, 169.3 ppm.

*3,3'-(4-Dimethylaminophenylmethylene)-bis-(4-hydroxycoumarin) (**4i**)*:

m.p.= 220-222 ˚C (Lit. [37]: m.p.= 222-224 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 3.16 (s, 6H), 6.32 (s, 1H), 7.23-7.30 (m, 6H), 7.45 (d, 2H, *J* = 8.4 Hz), 7.53 (t, 2H, *J* = 8.4 Hz), 7.84 (d, 2H, *J* = 8.4 Hz) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 36.5, 46.1, 103.5, 116.1, 120.1, 123.5, 124.6, 128.7, 131.7, 141.1, 143.8, 153.0, 165.0, 168.1 ppm.

*3,3'-(4-Hydroxyophenylmethylene)-bis-(4-hydroxycoumarin) (**4j**)*:

m.p.= 228-230 ˚C (Lit. [43]: m.p.= 193 ˚C). ^{1}HNMR (400 MHz, $CDCl_3$): δ= 5.57 (brs, 1H, OH), 6.06 (s, 1H), 6.81 (d, 2H, *J* = 8.4 Hz), 7.09 (d, 2H, *J* = 8.4 Hz), 7.41-7.43 (m, 4H), 7.65 (t, 2H, *J* = 8.4 Hz), 8.03-8.07 (m, 2H), 11.32 (brs, 1H, OH), 11.50 (s, 1 H, OH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 35.5, 104.2, 105.7, 115.7, 116.7, 124.4, 125.0, 126.5, 127.7, 133.0, 152.4, 154.9, 164.7, 165.9, 167.1, 169.4 ppm.

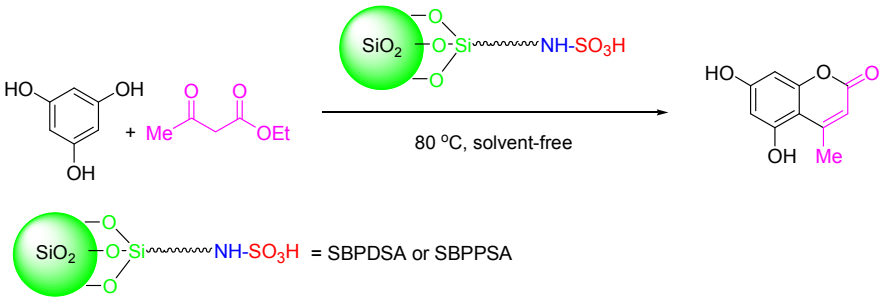
3. Results and Discussion

In continuation of our studies on the design and application of silica functionalized solid acid or base as catalyst in organic transformations [27-36], herein, we study the catalytic activity of SBPDSA in the synthesis of coumarins and biscoumarins.

To study the effect of catalyst loading on the condensation reaction of phenols and β-keto esters as the corresponding coumarins the reaction of floroglucinol (1,3,5-tri-hydroxyphenol) with ethyl acetoacetate was chosen as a model reaction (Scheme 2 and Table 1). To illustrate the need of catalyst for these reactions we examined the Pechmann reaction of floroglucinol with ethyl acetoacetate in the absence of these solid acid catalysts. In this case the reaction did not proceed even after 24 h (Table 1, entry 1).

Obviously, SBPDSA is an important reaction component. The optimal amount of SBPDSA was 0.05 g (4.9 mol%) per 1 mmol of phenol at 80 ˚C under solvent-free conditions. Although lower catalyst loading of 0.03 g (2.9 mol%) or 0.01 g (0.96 mol%) of SBPDSA accomplished this condensation, however, 0.05 g of SBPDSA per 1 mmol of phenol was optimum in terms of reaction time and isolated yield. Therefore, we employed the optimized conditions (0.05 g of SBPDSA at 80 ˚C under solvent-free conditions) for the condensation reaction of phenols with different *β*-keto esters to the corresponding coumarins (Scheme 3).

As shown in Table 2, different *β*-keto-esters such as methyl (**2a**), ethyl (**2b**), allyl (**2c**), and benzyl acetoacetate (**2e**) treated with phenolic substrates under optimized conditions gave corresponding products in high yields.

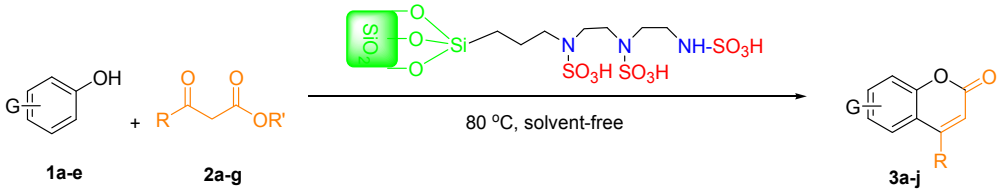


Scheme 2. Condensation of floroglucinol and ethyl acetoacetate catalyzed by SBPDSA or SBPPSA.

Table 1. Investigation of the effect of catalyst on the reaction of floroglucinol and ethyl acetoacetate.[a]

Entry	Catalyst	Catalyst loading (g)	Time (min)	Yield (%)[b]
1	No catalyst	-	24 h	-
2	SBPDSA	0.01	135	75
3	SBPDSA	0.03	40	86
4	SBPDSA	0.05	5	92
5	SBPDSA	0.07	5	92
6	SBPPSA	0.05	30	85
7	SBPPSA	0.07	10	93
8	SBPPSA	0.1	10	93

[a]Reaction conditions: floroglucinol (1 mmol), ethyl acetoacetate (1 mmol), at 80 ˚C under solvent-free conditions.
[b]Isolated Yield.

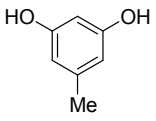
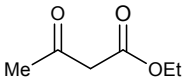
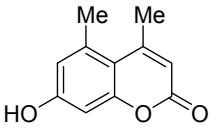
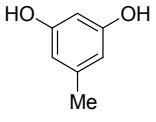
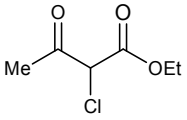
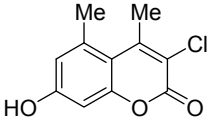
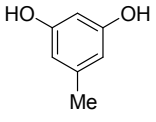
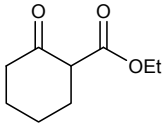
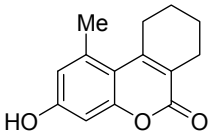
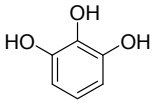
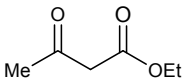
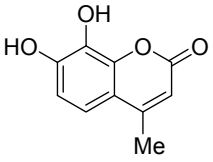
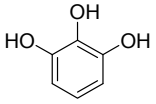
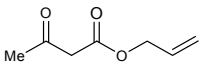
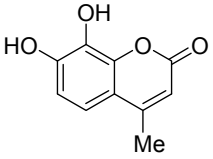
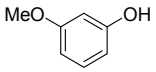
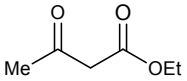
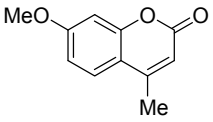
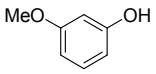
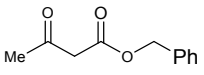
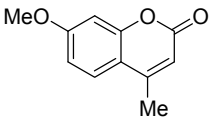


Scheme 3. Condensation reaction of phenols and *β*-keto esters catalyzed by SBPDSA.

Table 2. Synthesis of various coumarins in the presence of SBPDSA at 80 ˚C under solvent-free conditions.

Entry	Phenol	*β*-keto-esters	Product	Time (min)	Yield (%)[a]
1	**1a**	**2a**	**3a**	5	95
2	**1a**	**2b**	**3a**	5	92
3	**1a**	**2c**	**3a**	10	90
4	**1a**	**2e**	**3a**	10	91
5	**1a**	**2d**	**3b**	5	94
6	**1a**	**2f**	**3c**	10	93
7	**1a**	**2g**	**3d**	10	91
8	**1b**	**2b**	**3e**	10	90

Table 2. (*Continued).*

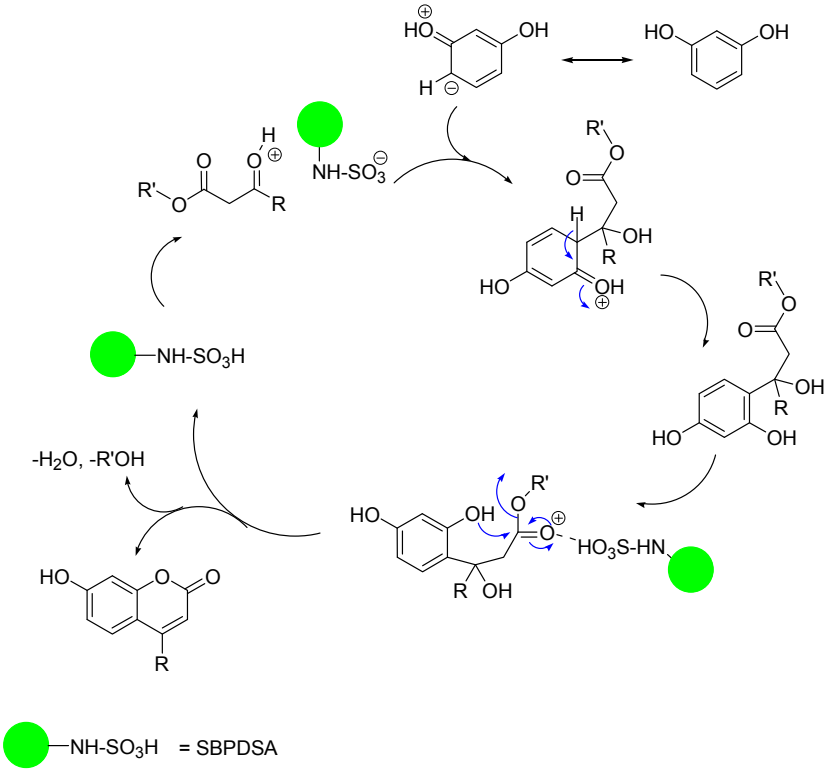
9	 **1c**	 **2b**	 **3f**	12	93
10	 **1c**	 **2d**	 **3g**	10	90
11	 **1c**	 **2f**	 **3h**	15	85
12	 **1d**	 **2b**	 **3i**	10	80
13	 **1d**	 **2c**	 **3i**	10	81
14	 **1e**	 **2b**	 **3j**	15	86
15	 **1e**	 **2e**	 **3j**	15	85

[a]Isolated yield.

Ethyl 2-chloroacetoacetate (**2d**) treated with floroglucinol (**1a**) and oricinol (**1c**) gave corresponding products **3b** and **3g** in 94% and 90% yields respectively (Table 2, entries 5,10). Ethyl 2-oxocyclohexanecarboxylate (**2f**) were reacted with floroglucinol (**1a**) and oricinol (**1c**) to give corresponding products **3c** and **3h** in high yields (Table 2, entries 6,11). Ethyl 3-oxohexanoate (**2g**) was converted to corresponding products **3d** in 91% yield (Table 2, entry 7).

The Pechmann condensation proceeds through transesterification followed by intramolecular hydroalkylation and dehydration [15,16]. These three steps are acid catalyzed reactions. A possible mechanism for the Pechmann condensation of phenols and *β*-keto ester by solid acid catalysts is presented in Scheme 4, which is also proposed by other workers [26].

The possibility of recycling the catalyst was examined using the reaction of floroglucinol (1 mmol) with ethyl acetoacetate (1 mmol) in the presence of SBPDSA (0.05 g) at 80 ˚C under solvent-free conditions. Upon completion, warm ethanol was added then the reaction mixture was filtered and the remaining solid was



Scheme 4. A plausible mechanism for the synthesis of coumarins using SBPDSA as catalyst.

washed with warm ethanol and the catalyst reused in the next reaction. The recycled catalyst could be reused four times without any additional treatment. No observation of any appreciable loss in the catalytic activity of SBPDSA was observed (Fig. 1).

Encouraged by these results, we tried to extend the scope of the catalytic activity of SBPDSA for condensation reaction of 4-hydroxycoumarins and aromatic aldehydes to afford biscoumarin derivatives (Scheme 5).

The desired 3,3'-(4-chlorophenylmethylene)-bis-(4-hydroxycoumarin) **4b** was obtained in 89% yield. This condensation reaction was carried out in refluxing ethanol, acetonitrile, and dichloromethane in 60%, 50%, and 30% yields respectively. Thereafter, a series of differently substituted biscoumarins were prepared successfully from different aromatic aldehydes bearing electron-withdrawing and electron-donating groups, 4-hydroxycoumarin in water and under reflux conditions. These results are listed in Table 3.

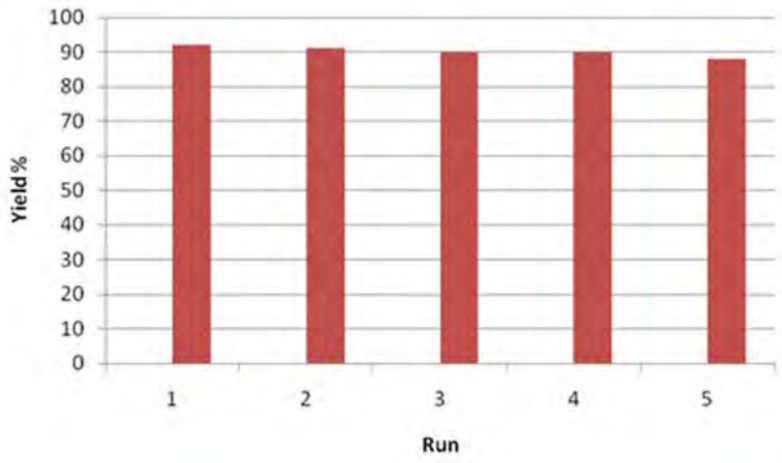
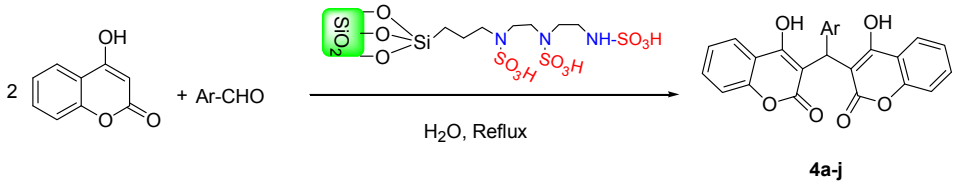


Fig. 1. Recyclability of SBPDSA (0.05 g) in the reaction of floroglucinol (1 mmol) with ethyl acetoacetate (1 mmol) under solvent-free conditions at 80 ˚C (t = 5 min).



Scheme 5. Synthesis of biscoumarin derivatives using SBPDSA as catalyst.

Table 3. SBPDSA catalyzed synthesis of biscoumarin derivatives.

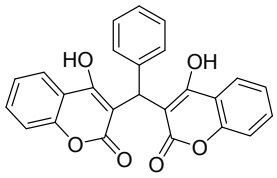
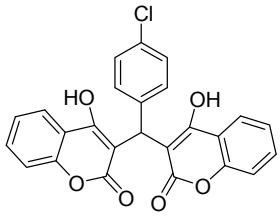
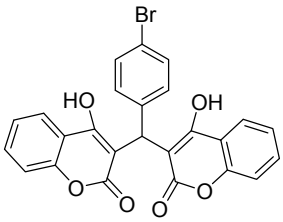
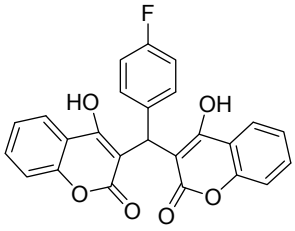
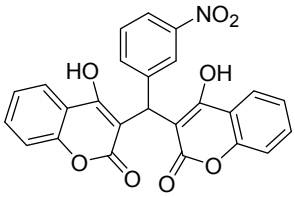
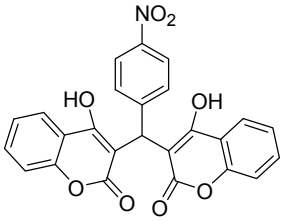
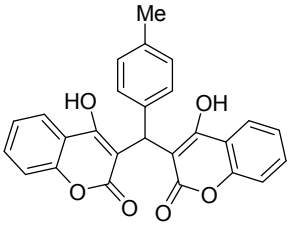
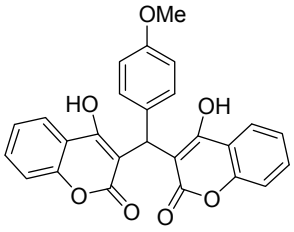
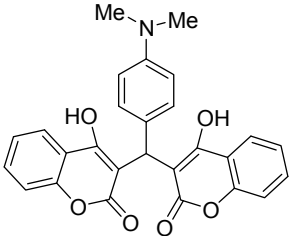
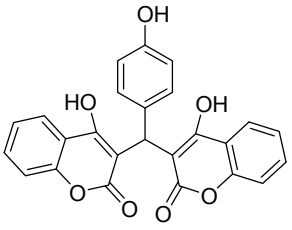
Entry	Ar	Product	Time (min)	Yield (%)[a]
1	C_6H_5-	 **4a**	180	93
2	4-Cl-C_6H_4-	 **4b**	90	89
3	4-Br-C_6H_4-	 **4c**	90	88
4	4-F-C_6H_4-	 **4d**	90	87
5	3-O_2N-C_6H_4-	 **4e**	120	89

Table 2. (*Continued).*

6	4-O_2N-C_6H_4-	 **4f**	90	88
7	4-Me-C_6H_4-	 **4g**	120	90
8	4-MeO-C_6H_4-	 **4h**	90	87
9	4-Me_2N-C_6H_4-	 **4i**	90	84
10	4-HO-C_6H_4-	 **4j**	100	90

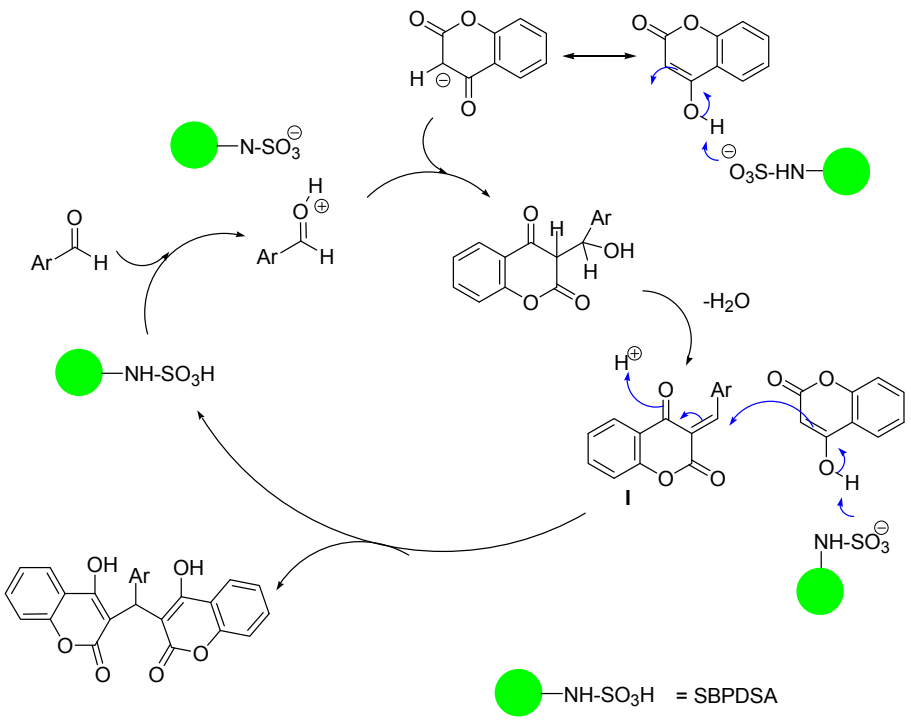
[a]Yield isolated of products.

A plausible mechanism in the presence of an acid according to Davoodnia [38] was drawn in Scheme 6. The carbonyl group of aldehyde activated in the presence of solid acid and condensed by 4-hydroxycoumarin to form intermediate **I**.

Subsequently, the intermediate **I** condensed via Michel attack with 4-hydroxycoumarin in the presence of solid acid to give the desired product.

4. Conclusions

We have shown that silica-bonded *n*-propyldiethylene-triamine (SBPDSA), which can be prepared from commercially available and cheap starting materials, catalyzed the synthesis of 2-amino-5-oxo-5,6,7,8-tetra hydro-4*H*-chromenes. The mild reaction conditions and simplicity of the procedure and reusability of catalyst are the advantages of this method.



Scheme 6. A plausible mechanism for synthesis of biscoumarins.

Acknowledgment

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