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Design, Characterization and Application of SO_3H-Functionalized Phthalimide as a Highly Efficient Catalyst for the Condensation of Dimedone with Arylaldehydes, β-Ketoesters and Ammonium Acetate

Z. Kordrostami*

Department of Chemistry, Payame Noor University, P. O. Box: 19395-3697, Tehran, Iran

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In this work, SO_3H-functionalized phthalimide (SFP) as a SO_3H-containing solid acid is prepared by the reaction of phthalimide with chlorosulfonic acid, and characterized by FT-IR, ^1H and ^{13}C NMR, Mass, TG, DTG, XRD and SEM. Then, it is utilized as a highly efficient, heterogeneous and green catalyst for the one-pot multi-component condensation of dimedone with arylaldehydes, β-ketoesters and ammonium acetate under solvent-free conditions to afford polyhydroquinolines in excellent yields and in short reaction times.

Keywords: SO_3H-functionalized phthalimide (SFP), SO_3H-containing solid acid, Dimedone, Arylaldehyde, β-Ketoester, Polyhydroquinoline

INTRODUCTION

In recent years, development of heterogeneous, easily recyclable and environmentally benign catalysts for synthesis of fine chemicals has attracted much attention. Solid acids are certainly an important class of the above-mentioned catalysts used to promote different organic transformations. Catalytic activity of solid acids depends on their strength, number of acidic sites, and Lewis/Brønsted acidity [1-10]. The advantages of solid acid catalysts in organic synthesis can be summarized as follows: (i) isolation of the product is simple, (ii) reaction is often performed under milder conditions, (iii) reaction selectivity often increases, (iv) atom efficiency of reaction is improved, (v) the process is simple, (vi) precious raw materials used for preparation of the catalysts lifetime (through reusing), (vii) volume of the waste is significantly reduced, and (viii) process is in agreement with the green chemistry protocols [1-10]. Another important goal in green chemistry is elimination of volatile organic solvents; in fact, solvent-free conditions make synthesis simpler, save energy, and prevent solvent waste, hazards and toxicity [3-10]. It is noteworthy that the combination of heterogeneous catalysis with the use of solvent-free conditions represents an appropriate route toward the so-called ideal synthesis [3-10].

Currently, there is a rapid growth in introducing acidic catalysts containing SO_3H group for the organic synthesis, because of their unique properties such as high reactivity, efficiency, ability to promote a wide range of reactions and easy access to the corresponding starting materials [4-10]. Multi-component reactions (MCRs) play a significant role in combinatorial chemistry since they can synthesize desired products with better efficacy and atomic economy in a single step from three or more starting materials. Furthermore, they decrease energy consuming steps such as separation and purification of intermediates, and improve raw materials consumption. MCRs also present the advantage of synthetic efficiency and simplicity compared with conventional chemical reactions [11-14].

The one-pot multi-component condensation of dimedone with arylaldehydes, β-ketoesters and ammonium acetate is of importance as this reaction provides a simple route toward polyhydroquinolines synthesis [15-26]. This class of organic compounds has various biological activities, such as antiatherosclerotic, hepatoprotective, vasodilatory, antitumor, geroprotective, bronchodilatory, and antidiabetic

*Corresponding author. E-mail: zr.kordrostami@gmail.com

properties, and some of them have been applied as calcium channel modulators and curatives for cardiovascular diseases [27-31]. They have been also utilized as chemosensitizers in tumor therapy, as neuroprotectants and platelet anti-aggregatory agents, and as cerebral anti-ischemic agents in the treatment of Alzheimer's disease [32,33]. Some catalysts have been employed to promote the synthesis of polyhydroquinolines, *e.g.* $Yb(OTf)_3$ [15], Co_3O_4-CNT [16], *L*-proline [17], *threo*-(1S,2S)-2-amino-1-(4′-nitrophenyl)-1,3-propanediol [18], CAN [19], sulfonic acid functionalized SBA-15 [20], ionic liquid or solid-supported ionic liquids [21,22], FeF_3 [23], triton X-100 [24], magnetic Fe_3O_4 nanoparticles [25] and palladium(0) nanoparticles [26]. Nevertheless, most of the reported methods and catalysts have one or more of the following drawbacks: (i) the use of large amount of catalyst, (ii) application of toxic or expensive catalysts, (iii) long reaction times, (iv) low yields, (v) harsh reaction conditions, (vi) tedious work-up procedure, (vii) reaction under certain special conditions, and (viii) poor agreement with the green chemistry protocols. So, looking for more efficient, green and inexpensive catalysts for the preparation of polyhydroquinolines under milder reaction conditions is still relevant.

Considering these issues, we currently report the synthesis of SO_3H-functionalized phthalimide (SFP), as a SO_3H-containing solid acid, from available and inexpensive reactants (phthalimide and chlorosulfonic acid), and its characterization using FT-IR, ^1H and ^{13}C NMR, Mass, TG (thermal gravimetric), DTG (differential thermal gravimetric), XRD (X-ray diffraction) and SEM (scanning electron microscopy) spectra. Then, we use SFP as a highly efficient, heterogeneous and reusable catalyst for the one-pot multi-component condensation of dimedone with arylaldehydes, β-ketoesters and ammonium acetate under solvent-free conditions to furnish polyhydroquinolines as biologically interesting compounds.

EXPERIMENTAL SECTION

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral reactions was monitored by TLC using silica gel SIL G/UV data with those reported in the literature. Progress of the 254 plates. The ^1H NMR (250, 300 or 500 MHz) and ^{13}C NMR (62.5, 75 or 125 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. TG and DTG were analyzed by a Perkin Elmer apparatus, Model: Pyris 1 (25 to 500 °C, temperature increase rate of 10 °C min^{-1}, nitrogen atmosphere).

Procedure for the Production of SFP

To a round-bottomed flask (50 ml) containing phthalimide (0.736 g, 5 mmol), was added chlorosulfonic acid (0.594 g, 5.1 mmol) dropwise at 10 °C. After the addition was completed, the reaction mixture was stirred at room temperature for 5 h, and then at 70 °C for 3 h. At the end of the process, the residue was washed with CH_2Cl_2 (2 × 10 ml), and dried to give SFP as a white solid in 98% yield. IR (KBr): 3350-2950, 1718, 1305, 1287, 1182, 1088, 1070 cm^{-1}. ^1H NMR (250 MHz, DMSO-d_6): δ 7.40-7.55 (m, 4H, aromatic hydrogens), 11.00 (s, 1H, OH of the SO_3H group). ^{13}C NMR (62.5 MHz, DMSO-d_6): δ 122.6, 132.0, 134.0, 169.0. Mass (m/z): 227 (M^+), 228 (M^++1), 210 (M^+-OH), 146 (M^+-SO_3H), 132 (M^+-NSO_3H), 104 (M^+-$CONSO_3H$) and 76 (M^+-$(CO)_2NSO_3H$).

General Procedure for the Synthesis of Polyhydroquinolines

SFP (0.023 g, 0.1 mmol) was added to a mixture of dimedone (0.14 g, 1 mmol), arylaldehyde (1 mmol), β-ketoester (1 mmol) and ammonium acetate (0.108 g, 1.4 mmol) in a test tube. The resulting mixture was firstly stirred magnetically at 60 °C, and after solidification of the reaction mixture, it was vigorously stirred with a small rod at the same temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature, CH_2Cl_2 (20 ml) was added, stirred for 3 min, and filtered to separate the catalyst (the product is soluble in CH_2Cl_2, while the catalyst is not soluble in this solvent). The filtrate was washed by H_2O (20 ml), and dried over Na_2SO_4. The solvent was evaporated to give the crude product which was purified by recrystallization from ethanol (95%) or column chromatography eluted with *n*-hexane/ethyl acetate. The recycled catalyst was washed by CH_2Cl_2, and used for the next run.

Selected Spectral Data of the Products

Ethyl-2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexa hydroquinoline-3-carboxylate (1). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 0.85 (s, 3H), 1.00 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H), 2.01-2.20 (m, 2H), 2.29 (s, 3H), 2.38-2.50 (m, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 4.82 (s, 1H), 7.05 (m, 1H), 7.18 (t, *J* = 6.7 Hz, 2H), 7.21 (t, *J* = 6.5 Hz, 2H), 9.12 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 14.5, 18.8, 26.8, 29.5, 32.6, 36.5, 50.6, 59.6, 103.4, 109.9, 113.5, 126.9, 128.8, 130.5, 146.0, 150.3, 167.0, 194.7.

Ethyl-2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6, 7,8-hexahydroquinoline-3-carboxylate (2). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.92 (s, 3H), 1.10 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 2.16 (d, *J* = 16.4 Hz, 2H), 2.24-2.29 (Distorted AB system, 2H), 2.41 (s, 3H), 4.07 (q, *J* = 7.1 Hz, 2H), 5.18 (s, 1H), 6.68 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl3): δ (ppm) 14.6, 19.8, 27.5, 29.8, 33.1, 37.7, 41.3, 51.0, 60.5, 105.3, 111.4, 123.7, 129.4, 145.0, 146.6, 149.6, 154.9, 167.3, 195.9.

Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3-carboxylate (4). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 0.85 (s, 3H), 1.00 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.96 (d, *J* = 16.0 Hz, 1H), 2.15 (d, *J* = 16.1 Hz, 1H), 2.27 (s, 3H), 2.37-2.49 (m, 2H), 3.66 (s, 3H), 3.97 (q, *J* = 7.0 Hz, 2H), 4.79 (s, 1H), 6.73 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3Hz, 2H), 8.99 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 14.6, 18.7, 26.9, 29.6, 32.6, 35.4, 50.6, 55.3, 59.4, 104.4, 110.7, 113.5, 128.8, 140.5, 145.1, 149.7, 157.7, 167.4, 194.7.

Ethyl-2,7,7-trimethyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexa hydroquinoline-3-carboxylate (5). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.96 (s, 3H), 1.08 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 2.15-2.31 (m, 7H), 2.35 (s, 3H), 4.09 (q, *J* = 7.1 Hz, 2H), 5.04 (s, 1H), 6.76 (s, 1H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, CDCl3): δ (ppm) 14.7, 19.7, 21.5, 27.6, 29.8, 33.1, 36.6, 41.3, 51.2, 60.2, 106.6, 112.4, 128.3, 129.0, 135.8, 143.9, 144.7, 149.3, 167.9, 196.1.

Ethyl-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3-carboxylate (6). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 0.86 (s, 3H), 1.00 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.96 (d, *J* = 16.0 Hz, 1H), 2.15 (d, *J* = 16.1 Hz, 1H), 2.26 (s, 3H), 2.36-2.49 (m, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 4.74 (s, 1H), 6.56 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 8.94 (s, 1H), 9.01 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 14.6, 18.7, 26.9, 29.6, 32.6, 35.3, 50.8, 59.4, 104.6, 110.8, 114.9, 128.8, 138.9, 144.8, 149.6, 155.7, 167.5, 194.7.

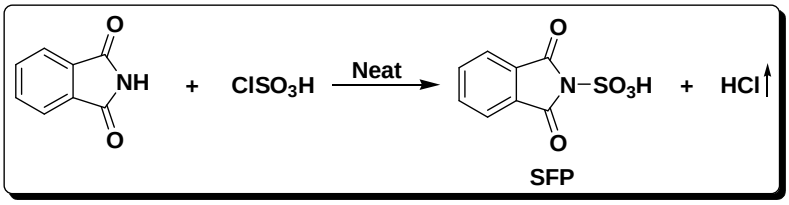
Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5, 6,7,8-hexahydroquinoline-3-carboxylate (7). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 0.83 (s, 3H), 0.99 (s, 3H), 1.10 (t, *J* = 6.9 Hz, 3H), 1.96 (d, *J* = 16.0 Hz, 1H), 2.16 (d, *J* = 16.1 Hz, 1H), 2.29 (s, 3H), 2.38-2.49 (m, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 4.84 (s, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 9.09 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 14.6, 18.8, 26.9, 29.5, 32.6, 36.2, 50.6, 59.5, 103.5, 110.1, 119.1, 130.2, 131.0, 145.8, 147.4, 150.0, 167.1, 194.7.

Methyl4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1, 4,5,6,7,8-hexahydroquinoline-3-carboxylate (12). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 0.84 (s, 3H), 0.99 (s, 3H), 1.97 (d, *J* = 16.0 Hz, 1H), 2.15 (d, *J* = 16.1 Hz, 1H), 2.28 (s, 3H), 2.37-2.49 (m, 2H), 3.52 (s, 3H), 3.66 (s, 3H), 4.81 (s, 1H), 6.73 (d, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 9.02 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 18.7, 26.9, 29.6, 32.6, 35.2, 50.7, 51.1, 55.3, 104.0, 110.7, 113.6, 128.7, 140.3, 145.4, 149.7, 157.7, 167.9, 194.7.

Methyl-4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6, 7,8-hexahydroquinoline-3-carboxylate (14). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 0.83 (s, 3H), 1.00 (s, 3H), 1.99 (d, *J* = 16.0 Hz, 1H), 2.18 (d, *J* = 16.1 Hz, 1H), 2.30 (s, 3H), 2.39-2.49 (m, 2H), 3.53 (s, 3H), 4.85 (s, 1H), 7.14-7.16 (m, 2H), 7.25-7.27 (m, 2H), 9.15 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 18.8, 26.8, 29.5, 32.6, 36.3, 103.1, 109.9, 121.6, 126.8, 129.1, 130.5, 130.6, 146.3, 150.3, 150.5, 167.5, 194.7; MS: m/z 404 (M+).

RESULTS AND DISCUSSION

Considering the unique properties of SO_3H-containing solid acidic catalysts, we decided to design SO_3H-functionalized phthalimide (SFP). For this purpose, phthalimide (1 eq.) was reacted with chlorosulfonic acid (1 eq.) to give SFP as a white powder (Scheme 1). In this section, we characterize the solid acid by studying its FT-IR, ^{1}H and ^{13}C NMR, TG, DTG, Mass, XRD and SEM spectra.



Scheme 1. The synthesis of SFP

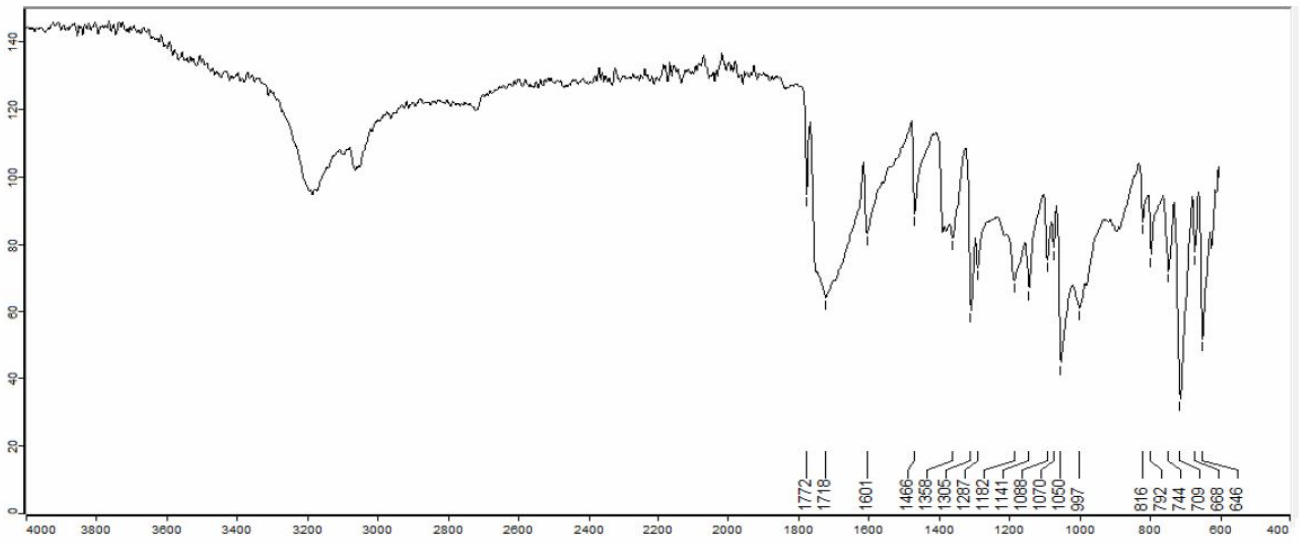


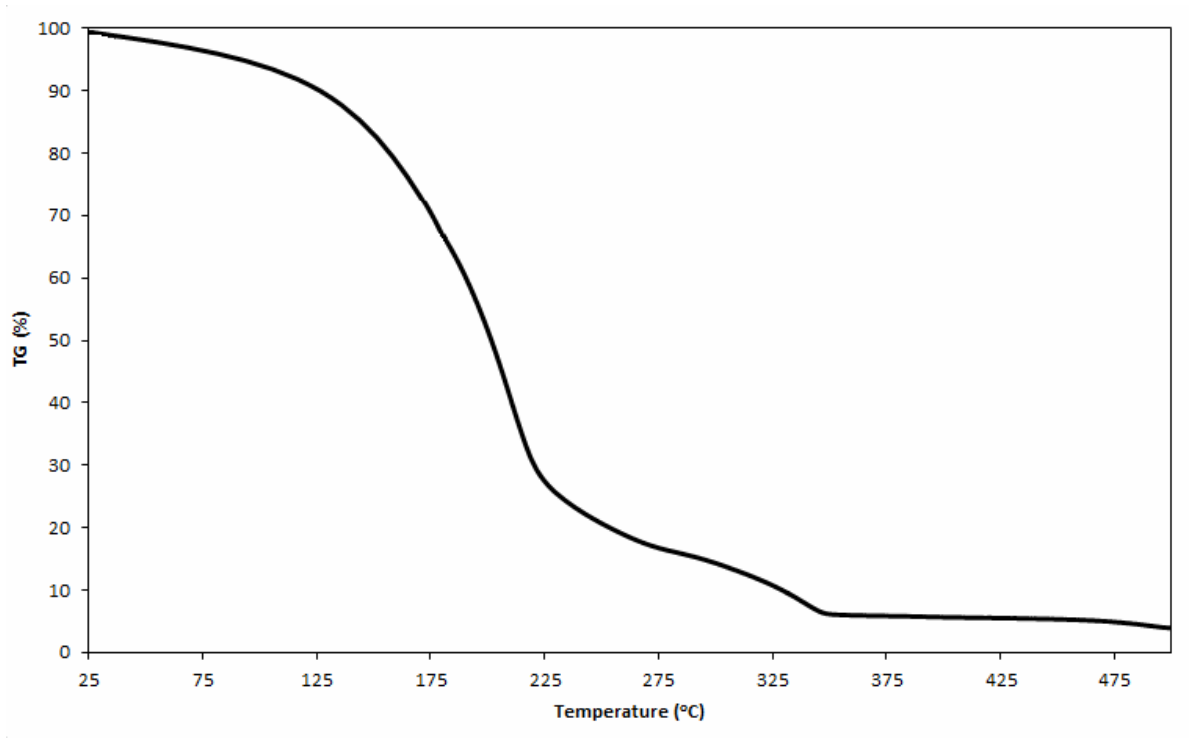
Fig. 1. FT-IR spectrum of SFP.

The FT-IR spectrum of SFP (Fig. 1), showed a broad peak at 2950-3350 cm^{-1} related to OH of the SO_3H group. The band at 1070 cm^{-1} was assigned to S-O-H bend. The strong peak at 1718 cm^{-1} corresponds to the carbonyl groups of the catalyst. Moreover, two peaks observed in 1088 cm^{-1} and 1305 cm^{-1} correspond to the vibrational modes of N-SO_2 bond. The strong absorptions at 1287 and 1182 cm^{-1} in the catalyst were assigned to the asymmetric and symmetric stretching and bending for S-O vibrations of SO_3H.

The ^{1}H NMR spectrum of SFP, showed a multiplet peak at 7.40-7.55 ppm corresponding to four aromatic hydrogens of the catalyst. The acidic hydrogen of SO_3H peak was observed at 11.00 ppm. To prove that this peak is really related to the hydrogen of SO_3H in the catalyst, we also recorded the ^{1}H NMR spectra of the starting materials for the preparation of SFP (*i.e.* phthalimide and chlorosulfonic acid) in DMSO-d_6. In these spectra, the acidic hydrogens' peaks were observed at 11.00 (for SFP), 11.31 (for phthalimide) and 13.54 (for $ClSO_3H$) ppm. The difference between the acidic hydrogens of SFP and its starting materials confirmed that phthalimide has been successfully reacted with chlorosulfonic acid to afford SFP. The peak observed at 11.00 ppm of the ^{1}H NMR spectrum of SFP, is really related to its SO_3H group, not acidic hydrogens of the unreacted starting materials, *i.e.* SO_3H of chlorosulfonic acid or NH of phthalimide.

The ^{13}C NMR spectrum showed three peaks in aromatic region (122.6, 132.0 and 134.0 ppm) corresponding to the four carbon types of the aromatic ring. Furthermore, a peak at 169.0 ppm concerns to the carbonyl groups.

Thermal gravimetric analysis of SFP was also studied at a range of 25-500 °C. The corresponding diagrams are



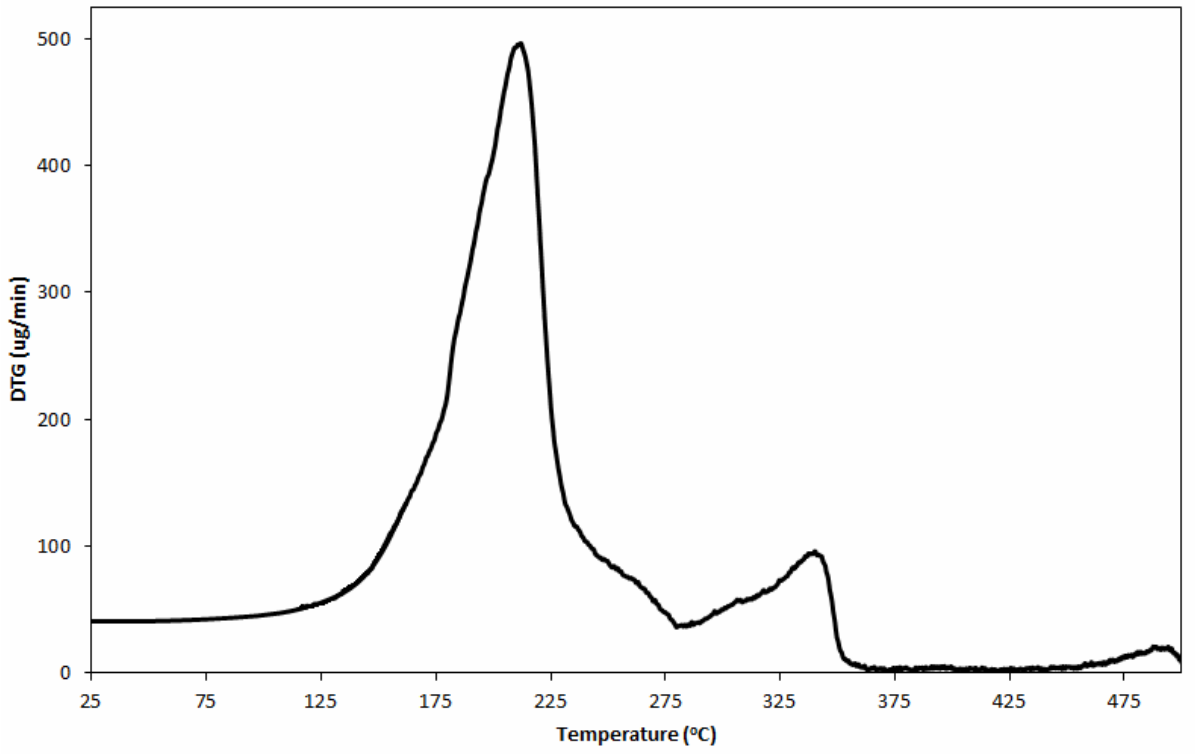


Fig. 2. The TG and DTG diagrams of SFP.

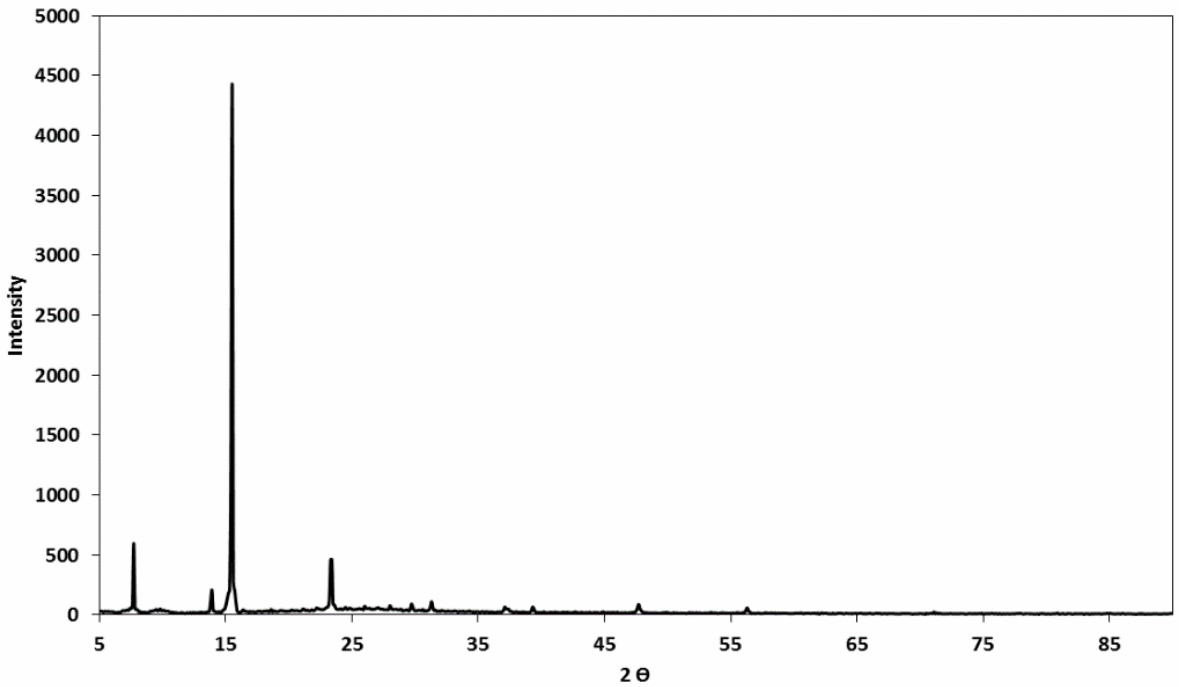


Fig. 3. The XRD pattern of SFP.

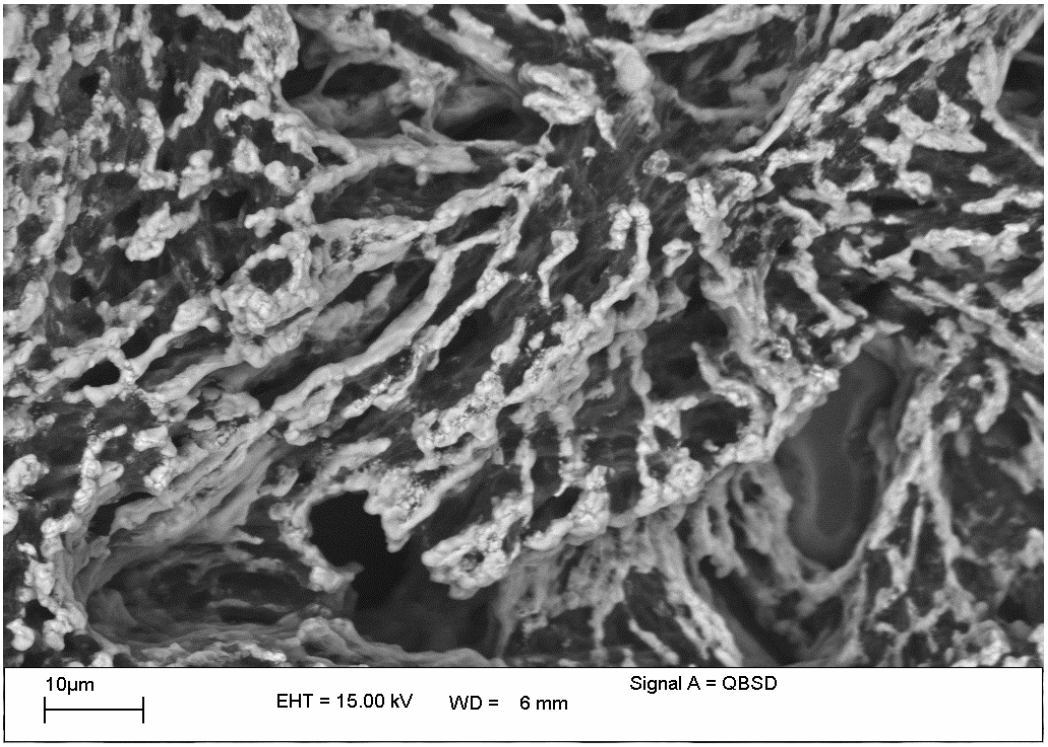
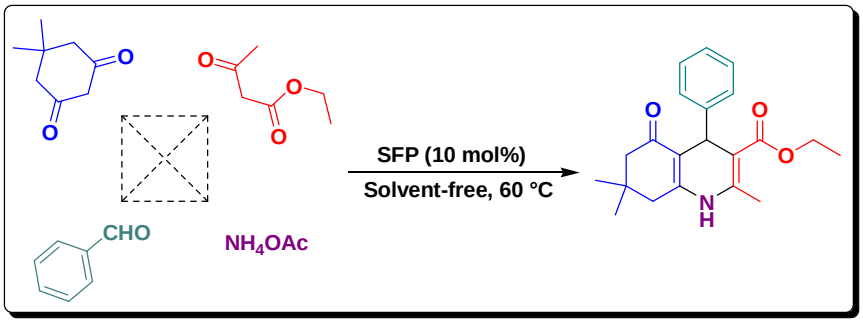


Fig. 4. The SEM image of SFP.



Scheme 2. The multi-component preparation of polyhydroquinolines catalyzed by SFP

Table 1. Effect of the Catalyst amount and Temperature on the Reaction between Dimedone, Benzaldehyde, Ethyl Acetoacetate and Ammonium Acetate

Entry	Catalyst (mol%)	Temp. (°C)	Time (min)	Isolated yield (%)
1	SFP (15)	60	30	90
2	SFP (10)	60	12	98
3	SFP (5)	60	25	91
4	SFP (10)	50	20	75
5	SFP (10)	70	15	80
6	$ClSO_3H$ (10)	60	12	60
7	Phthalimide (10)	60	12	67

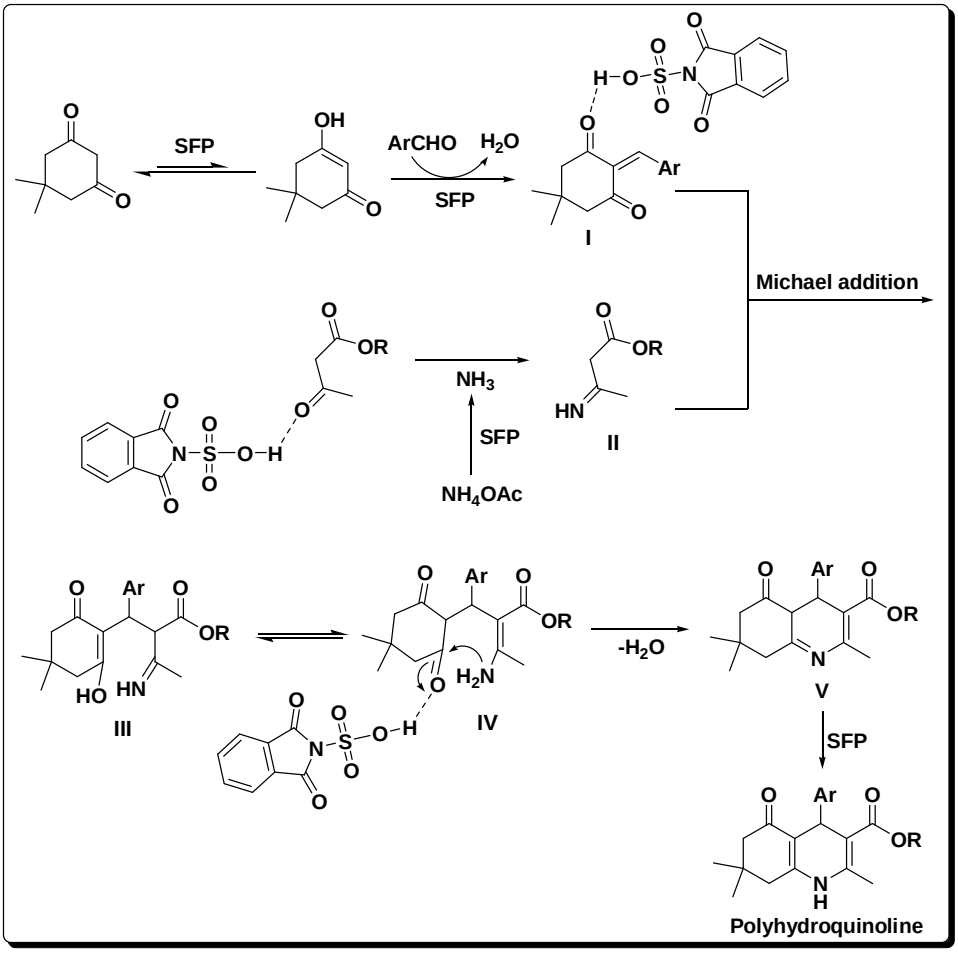
shown in Fig. 2. The thermal gravimetric (TG) and derivative thermogravimetry (DTG) diagrams showed weight losses in two steps, at about 150 to 220 °C, and 275 to 360 °C.

The XRD pattern of SFP shown in Fig. 3, exhibite four main peaks at 2θ = 7.70, 13.90, 15.50 and 23.30. The peaks width, particle sizes and interplaner distances resulted from the XRD pattern are indicated in Table 1. The crystallite sizes (D) of some particles calculated using the Debye-Sherrer formula ($D = K\lambda/(\beta\cos\theta)$, where λ is the X-ray wavelength, K is the Scherrer constant, β is the peak width of half-maximum, and θ is the Bragg diffraction angle), were 53, 71, 143 and 144 nm.

The SEM image of the catalyst is also indicated in Fig 4. The XRD and SEM results confirmed the crystal form of SFP. Moreover, the SEM image showed that the particles have not agglomerated, and the crystals have no high regular forms.

In the mass spectrum of the catalyst (Fig. 5), the peaks observed in m/z = 227 and 228, are related to the molecular mass (M^+) and M^++1. The other peaks that help to characterize the catalyst include 210 (M^+-OH), 146 (M^+-SO_3H), 132 (M^+-NSO_3H), 104 (M^+- $CONSO_3H$) and 76 (M^+-$(CO)_2NSO_3H$).

After the full characterization of the catalyst, we examined it to catalyze the synthesis of



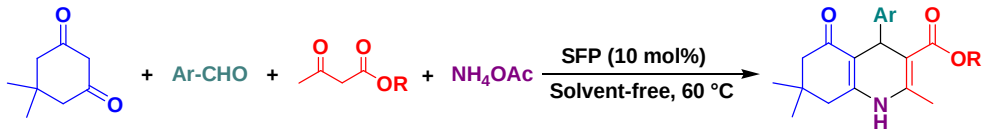
Scheme 3. The proposed mechanism for the synthesis of polyhydroquinolines using SFP

polyhydroquinolines.

First of all, we selected the condensation between dimedone (1 mmol), benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.4 mmol) as a model reaction (Scheme 2), and studied effect of the catalyst amount and temperature on the reaction. The results are displayed in Table 1. As clearly seen in Table 1, higher yield and shorter reaction time concern to 10 mol% of SFP at 60 °C (Table 1, Entry 2). Increasing the reaction time or the catalyst amount decreased the yield. In another study, to verify that the reaction of $ClSO_3H$ with phthalimide is completely progressed to give SFP, the model reaction was also checked in the presence of 10 mol% of $ClSO_3H$ or phthalimide (Table 1, Entries 6 and 7). The starting materials afforded the product in lower yields compared with SFP. These results also showed that phthalimide and $ClSO_3H$ are completely converted to SFP, and this solid acid is the real catalyst of the reaction.

To evaluate the efficiency and the generality of the catalyst, we reacted dimedone with various arylaldehydes (possessing electron-withdrawing groups and electron-donating groups), β-ketoesters (ethyl and methyl acetoacetate) and ammonium acetate under the optimal reaction conditions. The corresponding results are summarized in Table 2. As Table 2 indicates, all reactions proceeded efficiently to afford the desired polyhydroquinolines in high yields and in short reaction times. Thus, our solid acid, SO_3H-functionalized phthalimide, is a highly efficient and general catalyst to promote a reaction that needs an acidic catalyst, *i.e.* the

Table 2. The Solvent-free Synthesis of Polyhydroquinolines from Dimedone, Arylaldehydes, β-ketoesters and Ammonium Acetate Catalyzed by SFP at 60 °C



Product	Ar	R	Time (min)	Isolated yield (%)[a]	M.p. (°C)
1	C_6H_5	CH_3CH_2	12	98	201-203 (203-205) [18]
2	*p*-$O_2NC_6H_4$	CH_3CH_2	30	93	244-246 (247-249) [21]
3	*m*-$O_2NC_6H_4$	CH_3CH_2	35	90	179-181 (177-179) [18]
4	*o*-$O_2NC_6H_4$	CH_3CH_2	30	92	206-207 (208-211) [17]
5	*p*-$CH_3OC_6H_4$	CH_3CH_2	9	97	256-258 (255-257) [21]
6	*p*-$CH_3C_6H_4$	CH_3CH_2	11	97	261-263 (260-261) [15]
7	*p*-HOC_6H_4	CH_3CH_2	18	98	231-233 (232-234) [15]
8	*p*-$(CH_3)_2NC_6$	CH_3CH_2	25	90	228-230 (229-231) [18]
9	*p*-BrC_6H_4	CH_3CH_2	16	97	252-254 (255-257) [18]
10	*m*-BrC_6H_4	CH_3CH_2	20	94	233-235 (235-237) [18]
11	*p*-ClC_6H_4	CH_3CH_2	14	98	242-244 (243-245) [18]
12	*m*-ClC_6H_4	CH_3CH_2	23	98	230-232 (234-235) [19]
13	C_6H_5	CH_3	10	93	259-261 (260-262) [21]
14	*m*-$O_2NC_6H_4$	CH_3	5	85	230-232 (229-231) [21]
15	*p*-$CH_3OC_6H_4$	CH_3	10	90	256-258 (257-259) [21]
16	*p*-$CH_3C_6H_4$	CH_3	9	98	281-283 (281-283) [21]
17	*m*-BrC_6H_4	CH_3	12	95	222-224 (221-223) [21]
18	*p*-ClC_6H_4	CH_3	18	97	223-225 (220-222) [23]

preparation of polyhydroquinolines.

In a proposed mechanism (Scheme 3), we suggest that at first, dimedone is converted to its enol form in the presence of SFP. The enol form is condensed with aldehyde to give alkylidenedimedone I. On the other hand, the activated β-ketoester (by SFP) and ammonia react to afford imine II.

Afterward, Michael addition of II to I gives intermediate III. This intermediate is converted to IV by tautomerization, and intermediate IV gives V by intramolecular nucleophilic attack of the NH_2 group to the activated carbonyl group by the catalyst, and removal of one molecule H_2O. Subsequently, polyhydroquinonine is produced by tautomerization of intermediate V. The mechanism is confirmed by the literature [18,20,21].

CONCLUSIONS

In summary, we have introduced Brønsted solid acid, SO_3H-functionalized phthalimide, as a highly efficient, general and heterogeneous catalyst for the one-pot multi-component reaction between dimedone with aromatic aldehydes, β-ketoesters and ammonium acetate to afford polyhydroquinolones. The promising points for the presented protocols are efficiency, generality, high yields of the products, short reaction times, cleaner reaction profile, simplicity, low cost, ease of preparation and recycling of the catalyst.

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