Journal of Molecular Catalysis A: Chemical 374–375 (2013) 85–93

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Simultaneously application of SBA-15 sulfonic acid nanoreactor and ultrasonic irradiation as a very useful novel combined catalytic system: An ultra-fast, selective, reusable and waste-free green approach

Sadegh Rostamnia[a,*], Hongchuan Xin[b], Xiao Liu[c], Kamran Lamei[a]

[a] Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, P.O. Box 55181-83111, Maragheh, Iran
[b] Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China
[c] Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form 16 March 2013
Accepted 16 March 2013
Available online xxx

Keywords:
Combined catalytic system (US/SBA-15)
Ultrasonic irradiation
SBA-15/SO_3H
Green chemistry

ABSTRACT

Sonicated catalytically amount of the SBA-15/SO_3H nanoreactor with organic substrate was found to be an efficient, ultra-fast and waste-free green approach for the synthesis of the indazolophthalazinetriones, polyhydroquinolines and α-aminophosphonates as models of organic reactions. The advantages of present combined method are the use of a low scale catalyst, simple procedure with an easy filterable work-up method, waste-free, green and direct synthetic entry to excellent yield of products in a high reusability and a short reaction time. SBA-15 nanoreactor anchored covalently bonded $PrSO_3H$ organic groups, to produce organic–inorganic mesochannels, in reaction condition (combined ultrasound/nanoreactor system) as catalyst provide a synergistic means of an efficient approach of the reactants to acidic sites, and suitable mesochannels to drive out the products and water for next recycles.

1. Introduction

The 'greening' of global chemical processes has became a major issue in the chemical industry and biology both in terms of selection of reactions and for the study of solvent and catalyst effects [1]. The development of new strategies for recycling catalysts, which minimizes the consumption of auxiliary substances, energy and time required in achieving separations can result in significant economic and environmental benefits [2,3]. Green chemistry aims to eliminate pollution by preventing it from happening in the first place and by using resources for chemical products that are renewable [3].

Functionalized mesoporous silica with their nano-channels has shown catalytic performance because of their high surface area, low densities, high thermal and mechanical stability as a result of small nanoparticle sizes [4]. Incorporating the covalently bonded Brønsted sulfonic acid functionality into the SBA-15 mesoporous silicas (SBA-15/SO_3H) are of particular interest in organic synthesis, environmental chemistry and industry because of its high selectivity and high yielding abilities, and also heterogeneity and reusability capacities based on green chemistry desires [5]. In other hand, applications of the ultrasound have been demonstrated for their potential applications in the field of organic synthesis, green chemistry and industry [6]. Compared with traditional methods, this method is more convenient and easily controlled [6]. A large number of organic reactions can be carried out in a higher yield, shorter reaction time or milder conditions under ultrasonic irradiation (Fig. 1).

Compared with ultrasound-promoted reactions or catalytically applications of zeolite-type porous materials, only a limited paper has been reported for application of the combined ultrasound/nanoreactor system. However, many of these used montmorillonite clays and thin thickness MCM-41 material [7]. For practical applications, the hydrothermal and solvothermal stability of the catalyst is very important because most of the acid catalyzed organic reactions always involve water in high temperature [5]. Hydrothermally stable SBA-15 nanoreactor anchored covalently bonded sulfonic acid to aim organic–inorganic mesochannels in reaction condition as catalyst provide a synergistic means of an efficient approach of the reactants to acidic sites, and suitable mesochannels to drive out the products and water for next recycles [5]. On the other hand, based on green chemistry desires, the development of new strategies for recycling catalysts, which minimizes the consumption of auxiliary substances, energy and time required in achieving separations can result in significant economic and environmental benefits [8]. In the field of catalytic organic synthesis, many of this process have drawbacks such as low yields of products without any recycle, long reaction times, harsh reactions

* Corresponding author. Tel.: +98 9124338696.
E-mail addresses: srostamnia@gmail.com, rostamnia@maragheh.ac.ir (S. Rostamnia).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.03.017

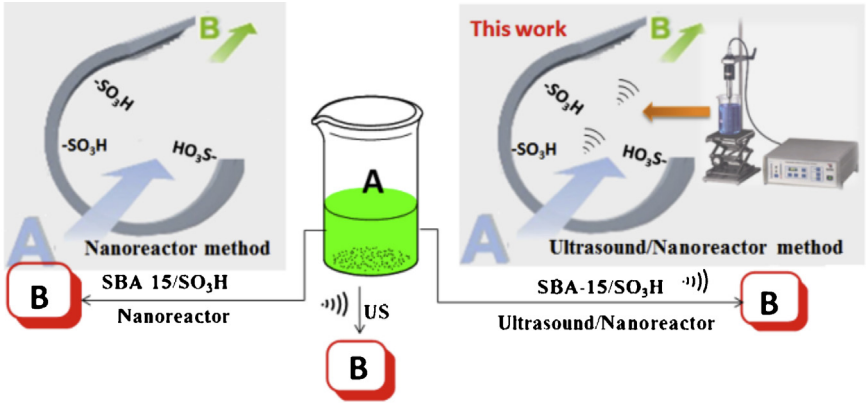


Fig. 1. Proposed reaction pathways.

conditions, tedious work-ups leading to the generation of large amounts of toxic metal or organic-containing waste, the requirement for an inert atmosphere and the use of stoichiometric or relatively expensive reagents [6–8]. As a result, the challenge in this field, was developing waste-free and effective green approach.

As part of our ongoing program [9], we are interested in the development of efficient and environmentally benign methods in synthetic organic chemistry. Our aim has been to investigate designing of the catalyst and energy sources to accomplish the desired chemical transformations with minimum by-products or waste generation, as well as to decrease reaction time using ultrasound and porous catalysts. Based on our earlier success in the green application of the ultrasonic in organic synthesis [6f], we could combine our achievements in nanocatalyst area [9c,i,j], with ultrasound. Here, we present the results of an extended investigation on the activity of the sulfonic acid functionalized mesoporous nanoreactor (SBA-15/SO_3H) as an ultra-fast, waste-free, green approach to synthesis of the heterocycles indazolophthalazinetriones **4**, polyhydroquinolines **8** and α-aminophosphonate **11** via multicomponent couplings.

2. Experimental

2.1. Chemicals and apparatus

All reagents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. The IR spectra were determined using a FT-IR Bruker-Vector 22. Melting points were measured on an Electrothermal 9100 apparatus. A multi-wave ultrasonic generator (Sonicator_3000; Misonix Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating as continues irradiation with a maximum power output of 600 W, was used for the ultrasonic irradiation. Frequencies below 50 kHz are generally preferred for the heterogeneous systems due to the more intense mechanical effects. Hence, we selected 19.6 kHz for sonication. Progress of reactions was monitored by Thin Layer Chromatography (TLC). ^1H and ^{13}C NMR spectra were measured ($CDCl_3$) with a Bruker DRX-300 AVANCE spectrometer at 300 and 75 MHz, respectively.

2.2. General procedures

Synthesis of SBA-15/SO_3H (SI): The synthesis of SBA-15-PrSO_3H has been achieved using three main steps: first step for preparation of the SBA-15 which known procedure described by Zhao et al. Second, which is thiol functionalization of the SBA-15 and third is oxidation of the SBA-15-Pr-SH to SBA-15-Pr-SO_3H by hydrogen peroxide (Fig. 2).

Temperature and solvent volume in ultrasonic method: it is to be noted here that when substrates and catalyst were added to the solution and irradiated, during the sonication the reaction temperature raised from its initial value and here the temperature was not controlled or fixed (maximum fluctuation range 3–10 °C). And, also, volume of solution during reaction progresses was adjusted by adding solvent using a syringe.

2.3. General procedure for synthesis of 3,3-dimethyl-13-aryl-2,3,4,6,11,13-hexahydro-1H-indazolo[1,2-b]phthalazine-1,6,11-trione derivatives **4**

A mixture of aldehyde (3.3 mmol), dimedone (3 mmol), phthalhydrazide (3 mmol), and SBA-15/SO_3H (0.07 g, ~4 mol%) was

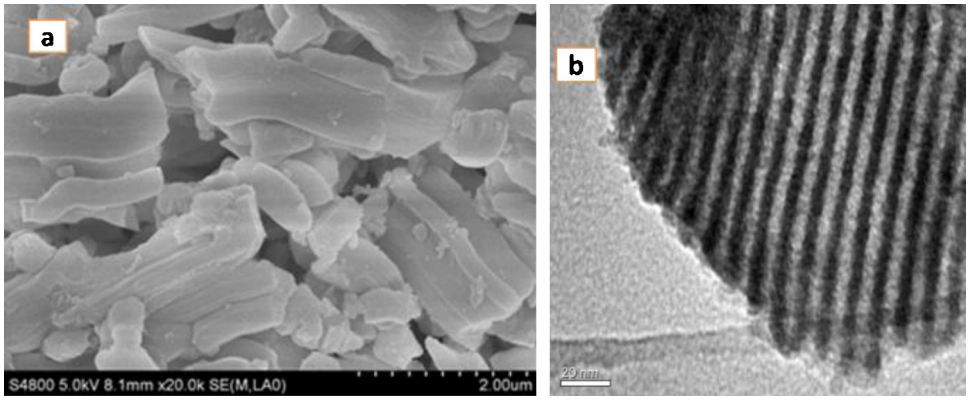


Fig. 2. SEM (a) and TEM (b) images of SBA-15/SO_3H nanoreactor.

heated at 45 °C (initial temperature value) for 15–20 min under irradiation of the ultrasonic in 10 mL EtOH. After completion of the reaction (TLC) the solvent was removed under reduced pressure, and the residue was added diethyl ether (2 × 15 mL) and filtered it for remove catalyst. The crude product was recrystallized from ethyl acetate/n-hexane (3:5) to afford the pure product. Products are known compounds, and their structures were deduced by comparison of their physical and spectroscopic data with those previously reported [2–12].

3,3-dimethyl-13-phenyl-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4a**): ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.22 (6 H, s), 2.34 (2 H, s), 3.21–3.45 (2 H, ABq, $^2J_{HH}$ 18.9 Hz), 6.45 (1 H, s), 7.27–7.43 (4 H, m), 7.83–7.86 (2 H, m), 8.25–8.37 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.5, 28.7, 34.7, 38.0, 50.9, 64.9, 118.6, 127.1, 127.7, 127.9. 128.7, 28.9, 129.0, 133.5, 134.5, 136.4, 150.8, 154.3, 156.0, 192.1.

13-(2-chlorophenyl)-3,3-dimethyl-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4b**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.21 (6 H, s), 2.32 (2 H, s), 3.20–3.44 (2 H, ABq, $^2J_{HH}$ 20.3 Hz), 6.68 (1 H, s), 7.21–7.33 (4 H, m), 7.84–7.87 (2 H, m), 8.24–8.39 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.4, 28.8, 34.8, 38.0, 50.9, 64.1, 127.2, 127.7, 128.1, 128.7, 129.0, 129.8, 130.5, 133.0, 133.6, 134.5, 151.8, 154.2, 156.2, 192.1.

13-(2-bromophenyl)-3,3-dimethyl-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine 1,6,11-trione (**4c**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.22 (6 H, s), 2.32 (2 H, s), 3.21–3.43 (2 H, ABq, $^2J_{HH}$ 18.9 Hz), 6.71 (1 H, s), 7.12–7.54 (4 H, m), 7.84–7.87 (2 H, m), 8.24–8.38 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.6, 28.7, 34.6, 38.0, 50.9, 65.7, 126.9, 127.7, 127.8, 128.0, 128.7, 129.1, 130.1, 133.6, 133.9, 134.5, 151.9, 154.3, 156.2, 192.0.

3,3-dimethyl-13-(2-nitrophenyl)-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4d**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.18 (6 H, s), 2.26–2.38 (2 H, ABq, $^2J_{HH}$ 19.2 Hz), 3.21–3.47 (2 H, ABq, $^2J_{HH}$ 20.3 Hz), 7.32–7.57 (4 H, m), 7.82–7.93 (2 H, m), 8.22–8.37 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.5, 28.6, 34.6, 38.0, 50.7, 60.5, 116.8, 125.1, 127.7, 128.1, 128.6, 129.0, 129.5, 130.7, 133.1, 133.8, 134.7, 149.2, 152.0, 154.4, 156.0, 191.9.

3,3-dimethyl-13-(3-nitrophenyl)-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4e**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.23 (6 H, s), 2.35 (2 H, s), 3.24–3.47 (2 H, ABq, $^2J_{HH}$ 19.2 Hz), 6.52 (1 H, s), 7.53–7.59 (1 H, m), 7.87–7.91 (3 H, m), 8.15–8.18 (2 H, m), 8.24–8.40 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.4, 28.7, 34.8, 38.0, 50.8, 64.2, 117.2, 121.5, 123.7, 127.7, 128.3, 128.6, 128.9, 129.7, 133.9, 134.3, 134.8, 138.6, 148.5, 151.8, 154.7, 155.9, 192.1.

13-(3-bromophenyl)-3,3-dimethyl-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4f**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.21 (6 H, s), 2.34 (2 H, s), 3.20–3.44 (2 H, ABq, $^2J_{HH}$ 19.2 Hz), 6.39 (1 H, s), 7.19–7.24 (1 H, m), 7.40–7.48 (3 H, m), 7.85–7.88 (2 H, m), 8.25–8.38 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.5, 28.6, 34.7, 38.0, 50.9, 64.2, 117.9, 122.8, 126.3, 127.8, 128.1, 128.9, 129.0, 129.8, 130.2, 131.9, 133.7, 134.7, 138.7, 151.2, 154.4, 156.0, 192.0.

3,3-dimethyl-13-(4-nitrophenyl)-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4g**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.18 (6 H, s), 2.33 (2H, s), 3.22–3.44 (2 H, ABq, $^2J_{HH}$ 18.9 Hz), 6.50 (1 H, s),7.60 (2 H, m), 7.86–7.89 (2 H, m), 8.17–8.25 (3 H, m), 8.35–8.39 (1 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.4, 28.7, 34.7, 38.0, 50.8, 64.8, 117.3, 124.0, 127.8, 128.1, 128.2, 128.6, 128.9, 133.9, 134.8, 143.4, 147.8, 151.7, 154.5, 155.9, 192.0.

13-(4-fluorophenyl)-3,3-dimethyl-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4h**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.21 (6 H, s), 2.34 (2 H, s), 3.20–3.44 (2 H, ABq, $^2J_{HH}$ 19.2 Hz), 6.43 (1 H, s), 7.02 (2 H, t, $^3J_{HH}$ 5.4 Hz), 7.38–7.43 (2 H, m), 7.84–7.87 (2 H, m), 8.25–8.37 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.5, 28.7, 34.7, 38.0, 50.9, 64.3, 115.5, 115.8, 118.21, 127.7, 128.0, 128.9, 129.0, 132.2, 133.6, 134.6, 151.0, 154.4, 156.0, 192.1.

13-(4-chlorophenyl)-3,3-dimethyl-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-*b*]phthalazine-1,6,11-trione (**4i**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.20 (6 H, s), 2.33 (2 H, s), 3.20 and 3.40 (2 H, ABq, $^2J_{HH}$ 19.2 Hz), 6.41(1 H, s), 7.29–7.38 (4 H, m), 7.84–7.87 (2 H, m), 8.24–8.37 (2 H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 28.4, 28.7, 34.6, 38.0, 50.6, 64.3, 118.0, 127.7, 128.0, 128.2, 128.5, 128.9, 129.7, 133.6, 134.5, 134.6, 134.9, 151.1, 154.3, 155.9, 192.1.

2.4. General procedure for synthesis of alkyl 4-(aryl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate derivatives **8**

To a solution of EtOH (10 mL) was added β-diketon (3 mmol), aldehyde (3.3 mmol), dimedone (3 mmol), ammonium acetate (4 mmol) and SBA-15/SO_3H (0.07 g, ∼4 mol%). The mixture was sonicated at room temperature (initial temperature value) for appropriate time and reaction progress monitored by TLC. After completion of the reaction, catalyst was filtrate by centrifuge and then the product recrystallized in ethanol. The products are known and were identified by their physical and spectral data.

Methyl 2,7,7-trimethyl-5-oxo 4-phenyl -1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8a**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.94 (s, 3 H), 1.09 (s, 3 H), 2.11–2.40 (m, 8 H), 3.62 (s, 3 H), 5.08 (s, 1 H), 7.08–7.31 (m, 5 H).

Methyl 4-(2-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8b**) IR (KBr ν_{max}/cm^{-1}): 3289, 2951, 1707, 1654, 1608, 1490, 1222, 1080, 1034, 827, 773, 540. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.91 (s, 3 H), 1.07 (s, 3 H), 2.04–2.36 (m, 7 H), 3.57 (s, 3 H), 5.38 (s, 1 H), 6.81 (s, 1 H), 7.00–7.34 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.19, 27.15, 29.37, 32.54, 35.61, 40.96, 50.62, 50.83, 105.17, 111.37, 126.42, 127.26, 129.61, 131.64, 131.64, 133.10, 143.87, 144.33, 148.92, 167.91, 195.51.

Methyl 4-(2-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8c**) IR (KBr ν_{max}/cm^{-1}) 3282, 3189, 3071, 2956, 1693, 1644, 1484. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.95 (s, 3 H), 1.09 (s, 3 H), 2.11–2.44 (m, 8 H), 3.62 (s, 3 H), 5.03 (s, 1 H), 5.90 (s, 1 H), 7.00–7.19 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 27.21, 29.37, 35.79, 41.23, 51.03, 127.66, 128.73.

Methyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8d**) IR (KBr ν_{max}/cm^{-1}): 3288, 2958, 1645, 1610, 1391, 1218, 1074, 1012, 840, 775, 538. ^{1}H NMR (300.13 MHz, CDCl3): 0.92 (s, 3 H), 1.08 (s, 3 H), 2.10–2.32 (m, 4 H), 2.39 (s, 3 H), 3.61 (s, 3 H, OCH3), 5.04 (s, 1 H), 6.2 (s, 1 H), 7.15–7.27 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.45, 27.06, 28.09, 28.24, 29.42, 32.71, 35.95, 41.05, 50.63, 51.08, 105.40, 111.90, 128.10, 129.24, 131.64, 143.98, 145.36, 148.23, 167.67, 195.57.

Methyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8e**) IR (KBr ν_{max}/cm^{-1}): 3274, 2960, 1705, 1648, 1608, 1494. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.94 (s, 3 H), 1.08 (s, 3 H), 2.10–2.38 (m, 7 H), 3.62 (s, 3 H), 3.74 (s, 3 H), 5.01 (s, 1 H), 5.95 (s, 1 H), 6.74 (d, J = 8.7 Hz, 2 H), 7.21 (d, J = 8.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.52, 27.16, 29.41, 35.40, 41.22, 50.68, 51.02, 55.10, 113.36, 128.75.

Ethyl 4-(2-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8f**) IR (KBr ν_{max}/cm^{-1}): 3245, 3078, 2958, 1701, 1600. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.95 (s, 3 H), 1.07 (s, 3 H), 1.22 (t, J = 6.9 Hz, 3 H), 2.13–2.34 (m, 10 H), 4.06 (q, J = 6.9 Hz, 2 H), 5.02 (s, 1 H), 6.30 (s, 1 H), 7.00–7.27 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.20, 19.31, 21.04, 27.21, 29.34, 32.74, 36.11, 41.05, 50.27, 59.85, 106.84, 112.01, 127.87, 128.63, 135.46, 143.08, 143.94, 167.38, 195.38.

Ethyl 4-(2-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8g**) IR (KBr ν_{max}/cm^{-1}): 3292, 3072, 2957, 1700, 1650, 1621, 1486, 758. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.89 (s, 3 H), 1.07 (s, 3 H), 1.17 (t, J = 6.9 Hz, 3 H), 1.65–2.35 (m, 7 H), 4.04 (q, J = 6.9 Hz, 2 H), 5.38 (s, 1 H), 6.11 (s, 1 H), 7.00–7.41 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.19, 19.35, 27.22, 29.32, 32.53, 35.97, 41.13, 50.57, 59.83, 105.33, 111.18, 126.24, 127.27, 129.67, 132.09, 133.20, 143.56, 148.68, 167.43, 195.35.

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8h**) IR (KBr ν_{max}/cm^{-1}): 3243, 3076, 2958, 1706, 1647, 1604, 1488, 844. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.92 (s, 3 H), 1.08 (s, 3 H), 1.17 (t, J = 6.9 Hz, 3 H), 2.10–2.38 (m, 7 H), 4.06 (q, J = 6.9 Hz, 2 H), 5.02 (s, 1 H), 6.25 (s, 1 H), 7.15–7.27 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.19, 19.38, 27.08, 27.76, 29.41, 32.69, 36.22, 41.00, 50.64, 59.90, 105.70, 111.77, 128.00, 129.44, 131.57, 143.79, 145.60, 148.51, 167.26, 195.60.

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8i**) IR (KBr ν_{max}/cm^{-1}): 3275, 3200, 3075, 2964, 1704, 1604, 1518, 1378. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.92 (s, 3 H), 1.10 (s, 3 H), 1.18 (t, J = 6.9 Hz, 3 H), 2.10–2.43 (m, 7 H), 4.05 (q, J = 6.9 Hz, 2 H), 5.16 (s, 1 H), 5.85 (s, 1 H), 7.47–8.10 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.17, 19.50, 27.06, 29.35, 32.74, 37.17, 41.10, 50.51, 60.08, 105.05, 111.19, 123.33, 128.95, 144.27, 146.24, 148.60, 154.26, 166.78, 195.26.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (**8j**) IR (KBr ν_{max}/cm^{-1}): 3300, 3078, 2950, 1648, 1610, 1032. ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.94 (s, 3 H), 1.07 (s, 3 H), 1.21 (t, J = 7.2 Hz, 3 H,), 2.13–2.29 (m, 4 H), 2.36 (s, 3 H), 3.74 (s, 3 H), 4.07 (q, J = 7.2 Hz, 2 H), 5.00 (s, 1 H), 6.14 (s, 1 H), 6.72–6.75 (m, 2 H), 7.20–7.27 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.22, 19.38, 27.17, 29.40, 32.72, 35.70, 41.07, 50.52, 55.10, 59.81, 112.26, 113.24, 129.00, 139.50, 143.02, 148.51, 157.80, 167.50, 195.53.

2.5. General procedure for synthesis of dialkyl anilino(aryl)methylphosphonate derivatives **11**

A mixture of aldehyde (5 mmol), amine (5 mmol), dimethyl phosphite (6 mmol) and SBA-15 (0.06 g, ~2 mol%) in EtOH (6.5 mL) was irradiated by ultrasound at room temperature (initial temperature value) for the required reaction time. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by simple filtration and the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). Evaporation of the solvent followed by purification on silica gel afforded pure α-aminophosphonates. All products were known and characterized by comparison of their physical and spectra data with those of already reported.

Dimethyl (4-chlorophenyl)(phenylamino)methylphosphonate (**11a**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 3.55 (d, $^3J_{HP}$ = 10.8, 3 H), 3.77 (d, $^3J_{HP}$ = 10.8, 3 H), 4.52 (br, 1 NH), 4.79 (d, $^2J_{HP}$ = 24.3, 1 H), 6.59–7.44 (m, 9 H).

Dimethyl phenyl(phenylamino)methylphosphonate (**11b**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 3.47 (d, $^3J_{HP}$ = 10.5, 3 H), 3.78 (d, $^3J_{HP}$ = 10.5, 3 H), 4.84 (d, $^2J_{HP}$ = 24.3, 1 H), 5.02 (br, 1 NH), 6.51–7.51 (m, 10 H).

Dimethyl (3-nitrophenyl)(phenylamino)methylphosphonate (**11c**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 3.64 (d, $^3J_{HP}$ = 10.8 Hz, 3 H), 3.83 (d, $^3J_{HP}$ = 10.4, 3H), 5.00 (d, $^2J_{HP}$ = 25.1, 1 H), 5.25 (br, 1 NH), 6.62–8.41 (m, 9 H).

Dimethyl (p-tolylamino)(2-chlorophenyl)methylphosphonate (**11d**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 2.16 (m, 3 H), 3.43 (d, $^3J_{HP}$ = 9.9, 3 H), 3.83 (d, $^3J_{HP}$ = 9.9, 3 H), 4.85 (br, 1 NH), 5.39 (d, $^2J_{HP}$ = 24.9, 1 H), 6.49–7.56 (m, 8 H).

Dimethyl (p-tolylamino)(4-nitrophenyl)methylphosphonate (**11e**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 2.24 (m, 3 H), 3.50 (d, $^3J_{HP}$ = 10.5, 3 H), 3.78 (d, $^3J_{HP}$ = 10.5, 3 H), 4.80 (d, $^2J_{HP}$ = 24.3, 1 H), 6.02 (br, 1 NH), 6.54–7.38 (m, 8H).

Dimethyl (p-tolylamino)(2-methoxyphenyl)methylphosphonate (**11f**) ^{1}H NMR (300.13 MHz, CDCl3): 2.18 (m, 3 H), 3.45 (d, $^3J_{HP}$ = 10.5, 3 H), 3.82 (d, $^3J_{HP}$ = 10.5, 3 H), 3.93 (s, 3 H), 4.06 (br, 1 NH), 5.43 (d, $^2J_{HP}$ = 24.0, 1 H), 6.54–7.49 (m, 8 H).

Dimethyl (N,N-diethylamino)(3-nitrophenyl)methylphosphonate (**11g**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 0.95 (t, J = 7.2 Hz, 6 H), 2.21 (m, 2 H), 2.88 (m, 2 H), 3.37 (d, $^3J_{HP}$ = 9.3 Hz, 3 H), 3.77 (d, $^3J_{HP}$ = 9.3 Hz, 3 H), 4.12 (d, $^2J_{HP}$ = 24.9 Hz, 1 H), 7.17–7.38 (m, 5 H).

Dimethyl (2-methoxyphenyl)(pyrrolidin-1-yl)methylphosphonate (**11h**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.69 (m, 4 H), 2.16 (m, 2 H), 2.64 (m, 2 H), 3.46 (d, $^3J_{HP}$ = 6.3 Hz, 3 H), 3.77 (d, $^3J_{HP}$ = 6.3 Hz, 3 H), 3.85 (s, 3 H), 4.66 (d, $^2J_{HP}$ = 18.0 Hz, 1 H), 6.89–7.75 (m, 4 H).

Dimethyl 1-(phenylamino)cyclohexylphosphonate (**11i**) ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.13–2.13 (m, 10 H), 3.45 (br, 1 NH), 3.55 (d, $^3J_{HP}$ = 10.5 Hz, 6 H), 6.66–7.06 (m, 5 H).

3. Results and discussion

Based on chemical and biological interests of indazolophthalazinetrione [10], for the synthesis of **4**, efficacy of different catalysts was studied. As expected, in which adduct of dimedone and aldehydes was treated with phthalhydrazide under the reaction conditions (Scheme 1), led to the products indazolophthalazinetriones **4**, arylmethylene bis(3 hydroxy-2-cyclohexene-1-one) **5** and heptahydroxanthenes **6** [11]. For our study, dimedone, benzaldehyde and phthalhydrazide were chosen as the benchmark substrates in the model reaction.

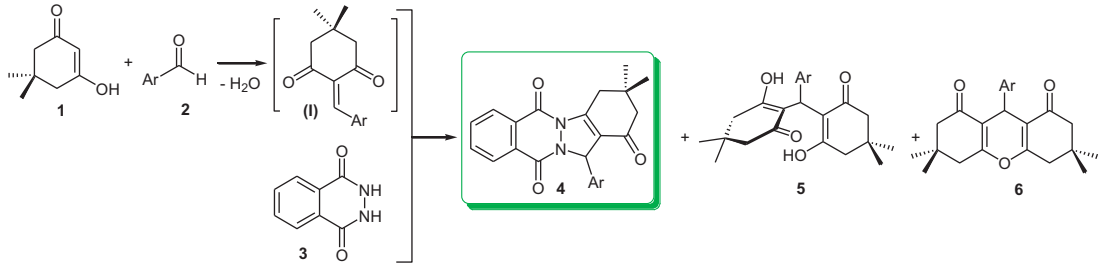
In model reaction, to obtain the desired product (**4a**), we tested the reaction using different catalysts. As shown in Table 1, the use of catalysts such as morpholine (entry 1), piperidine (entry 2), and iron oxide magnetic nanoparticles (entries 5–6) led to no desired product being obtained. Performing the reaction in the presence of sulfonic acid porous nanoreactor SBA-15 resulted in the production of **4a** in 45% yield with a trace amount of the side products **5a** and **6a** (entry 4) in compared of alternative core-shell structure (entry 7).

Next, due to the fact that the pore size of the nanoreactor may play an important role in the synthesis of **4a**, and based on our previous experience about ultrasonic effects in organic process and also in order to determine the evaluate the ultrasonic efficiency, in next step as comparative study efficacy of porous nanoreactor such as MCM-41/SO_3H and SBA-15/SO_3H catalyst was investigated via ultrasonic assisted (US), and high speed stirrer (HSS, 1500 rpm) method. The MCM-41/SO_3H with ~1.1 nm and SBA-15/SO_3H with ~5 nm pore size were chosen and investigated for the model reaction (SI). The synthesis of **4a** was carried out in MeCN during ultrasonic irradiation (US) and high speed stirrer (HSS). When the model reaction was run using SBA-15/SO_3H under sonicated condition, the product **4a** was obtained 87% yield at 60 °C during 0.25 h. The reaction rates and yields were enhanced by ultrasound (Fig. 3).

The model reaction was screened in different solvents using 6% mol of SBA-15/SO_3H (Table 2). When the reaction was run under sonicated condition in EtOH, the product was obtained in 96% yield at 65 °C in 25 min.

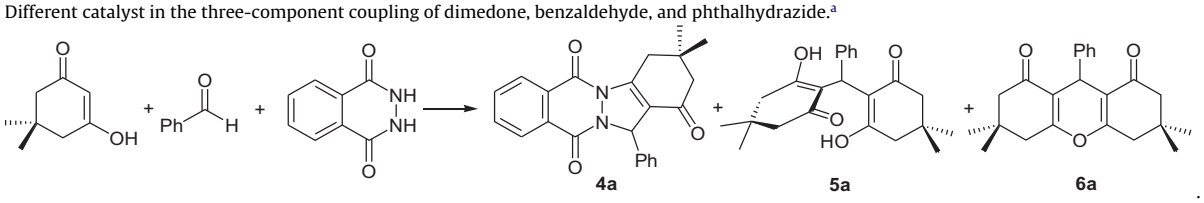
Next, the model reaction was carried out using different amounts of SBA-15/SO_3H as the catalyst (Fig. 4). A very high yield of 2*H*-indazolo[2,1-*b*]phthalazine-trione (96%) was obtained with 4 mol% of the catalyst. A further increase in the amount of catalyst (4–8 mol%) did not have any significant effect on the product yield or reaction time.

To the best of our knowledge, when the reaction was performed in DMSO, DMF and H_2O with 6 mol% of SBA-15/SO_3H under



Scheme 1. Expected products from the reaction of dimedone, aldehyde and phthalhydrazide.

Table 1
Different catalyst in the three-component coupling of dimedone, benzaldehyde, and phthalhydrazide.[a]



Entry	Catalyst	Temp (°C)	Time (h)	Yield%[b]		
				4a	**5a**	**6a**
1	$O(CH_2CH_2)_2NH$	Reflux	2	7	44	25
2	$(CH_2)_5NH$	Reflux	2	10	40	27
3	SBA-15/SO_3H	r.t.	1.5	T[d]	24	T[d]
4	SBA-15/SO_3H	Reflux	1.25	45	T[d]	T[d]
5	*nano*-Fe_3O_4	Reflux	2.5	T[d]	T[d]	75
6	γ-Fe_2O_3	Reflux	2.5	T[d]	T[d]	80
7	γ-Fe_2O_3@SiO_2/SO_3H[c]	Reflux	1.25	28	20	17

[a] Reaction conditions: dimedone (3 mmol), benzaldehyde (3.3 mmol), phthalhydrazide (3 mmol), catalyst (6 mol%) and MeCN (15 mL).
[b] Isolated yield.
[c] See Ref. [9j].
[d] Trace yield based on TLC analysis.

ultrasonic condition, although dimedone and benzaldehyde were almost consumed soon, but **4a** was formed with mixture of **5a**, **6a** and adduct **I**. When model reaction for synthesis of **4a** was carried out in ethanol by ultrasonic irradiation and high speed stirrer over 6 mol% catalyst, to our surprise in comparative study, the ultrasonic assisted method were completed during 15 min without any waste and side products (Table 2). The conversion for US method was 100% with 96% isolated yield while at the same reaction time, in HSS method conversion and yield was 63% and 45%, respectively.

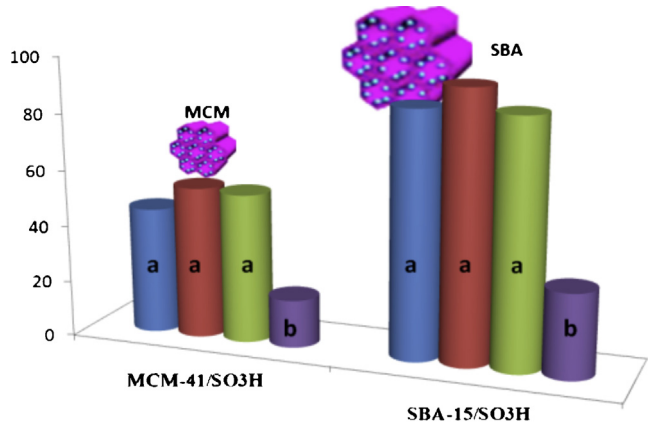


Fig. 3. Comprative study of the model reaction over porous nanoreactors: (a) US conditions: equal –SO_3H loaded (blue), equel surface area (red) and equel wieght (green) conditions. (b) HSS (violet) conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

To demonstrate the diversity of this combined ultrasonic and SBA-15/SO_3H catalytic system and to expand the scope of the process, the optimized conditions were applied to a series of 2*H*-indazolo[2,1-*b*]phthalazine-triones **4** via a three-component condensation of an aldehydes, dimedone and phthalhydrazide. The obtained results are summarized in Table 3.

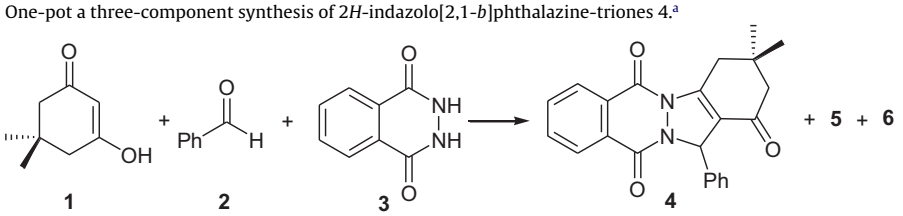
The possibility of recycling the SBA-15/SO_3H was also studied under sonicated condition. For practical applications of the SBA/SO_3H based on sonicated heterogeneous systems, the lifetime of the catalyst and its recovery are important factors. We therefore devised a set of experiments to recover and reutilize the SBA/SO_3H catalyst in the model coupling process. It can be seen that, the supported catalyst was highly reusable under the investigated reaction conditions, preserving almost unaltered its initial catalytic activity after seven uses. As comparison, SiO_2/OSO_3H and $HClO_4$/SiO_2 as the

Table 2
Study of the solvent and temperature on the model reaction.[a]

Solvent[b]	Temp (°C)[b]	Time (h)	Yield%[c] **4a**	
			HSS	US
DMF[e]	r.t	0.25	<10[d]	35
H_2O[e]	r.t	0.25	25	40
MeOH	r.t	0.25	18	20
EtOH	r.t	0.25	13	20
EtOH	60	0.25	45	96
CH_3CN	60	0.25	40	92
DMSO[e]	60	0.25	15	30

[a] Reaction scale: 3 mmol.
[b] Solvent: 5 mL.
[c] Isolated yield.
[d] Less than 10%.
[e] Contain **5a** and adduct **I**.

Table 3
One-pot a three-component synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones 4.[a]



Entry	Ar	Time (min)	Conv%[b]	Yield%[c]		
				4	**5**	**6**
1	C_6H_5	15	100	96 (**4a**)	N[d]	N[d]
2	2-Cl-C_6H_4	20	100	93 (**4b**)	N[d]	T[e]
3	2-Br-C_6H_4	20	100	92 (**4c**)	N[d]	T[e]
4	2-NO_2-C_6H_4	20	100	93 (**4d**)	N[d]	T[e]
5	3-NO_2-C_6H_4	18	100	94 (**4e**)	N[d]	N[d]
6	3-Br-C_6H_4	18	100	95 (**4f**)	N[d]	N[d]
7	4-NO_2-C_6H_4	15	100	96 (**4g**)	N[d]	N[d]
8	4-F-C_6H_4	15	100	93 (**4h**)	N[d]	T[e]
9	4-Cl-C_6H_4	15	100	95 (**4i**)	N[d]	N[d]

[a] Reaction scale: 3 mmol.
[b] Conversion calculated based on consume of dimedone (TLC).
[c] Isolated yield.
[d] No detected of the this product based on TLC analysis.
[e] Trace yield based on TLC analysis.

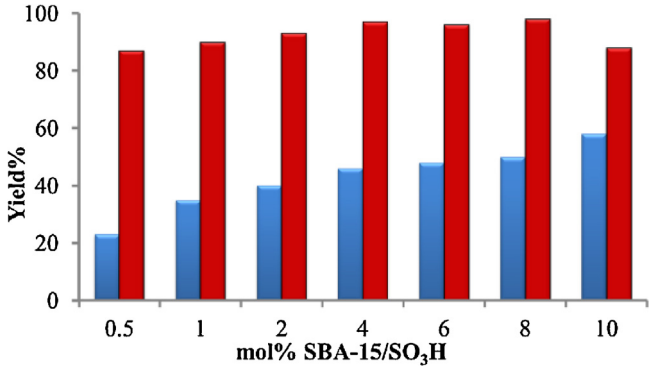


Fig. 4. Catalyst amounts study of SBA-15/SO_3H in combine ultrasound/nanoreactor system (blue for HSS) and (red for US). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

most relevant solid-acid catalysts have been investigated in same condition (Fig. 5).

These results clearly point out the efficiency of the proposed combined methodology (ultrasonic/nanoreactor) in both activity and recyclability of the high surface area mesoporous porous catalyst.

With these results in hand we decided to explore the scope of this method (ultrasonic/nanoreactor combined system). The catalytic activity of combined ultrasonic/nanoreactor system in the four-component synthesis of polyhydroquinolines [12], by the condensation of dimedone, aldehyde, β-dicarbonyl compound and ammonium acetate was also studied, in which adduct of dimedone and aldehyde was treated with 1,3-dicarbonyls in presence of the ammonium acetate under the reaction conditions, led to the products polyhydroquinolines **8**, and the molecules of **9**, **10** or **5**, **6** (Scheme 2).

Polyhydroquinolines are among the most fundamental and important bioactive systems in the various fields of organic chemistry [12]. Sonicated SBA-15 sulfonic acid have been considered candidates for the catalytically partner in the solid acid catalyzed four-component preparation of polyhydroquinolines 8. Four-component reaction of dimedone, benzaldehyde, methyl acetoacetate, and ammonium acetate was carried out using SBA-15 sulfonic acid as the catalyst, under ultrasonic irradiation and HSS method (Fig. 6). Methyl 4-(phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3 quinolinecarboxylate **8a** with 92% yield was obtained over 4 mol% of the SBA-15/SO_3H under sonicated conditions at room temperature. The expanded and obtained results are summarized in Table 4. It may be emphasized that in this green waste-free combined catalytically system not a trace of the byproducts **5**, **6** or **9**, **10** was observed in this reaction by TLC analysis.

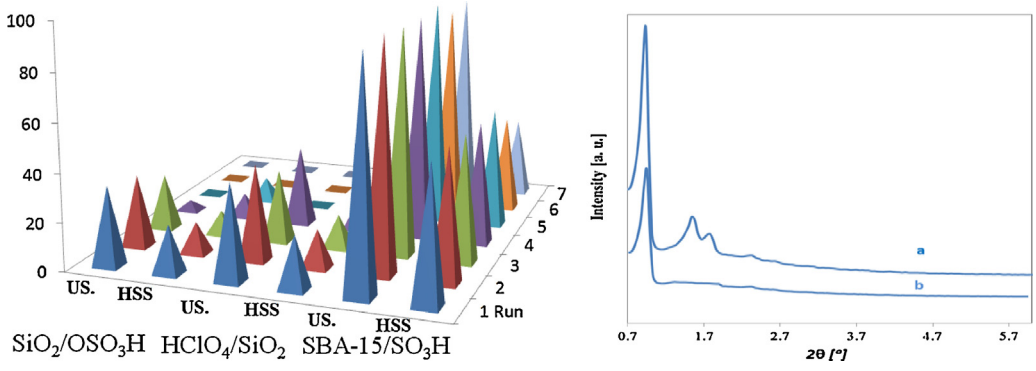
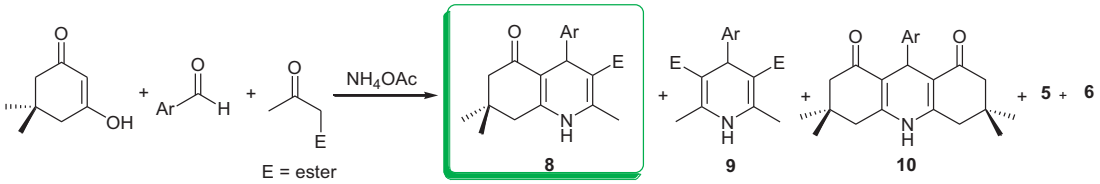
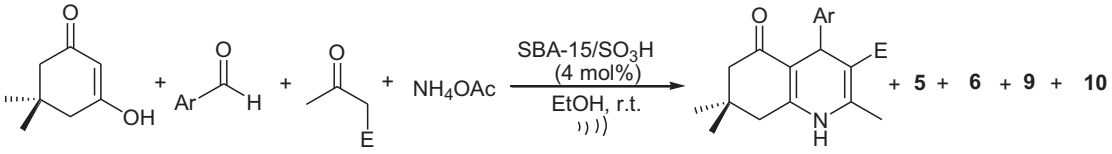


Fig. 5. Recyclability study on the synthesis of **4a** and XRD patterns of SBA-15/SO_3H: (a) newly prepared; (b) used 7 times.



Scheme 2. Synthesis of the polyhydroquinolines 8 and possible products.

Table 4
A clean one-pot synthesis of polyhydroquinolines 8.[a]



Entry	Ar	E	Time (min)	Conv%[b]	Yield%[c]				
					5	**6**	**8**	**9**	**10**
1	C_6H_5	CO_2Me	25	100	T[e]	N[d]	92 (**8a**)	~4	N[d]
2	2-Cl-C_6H_4	CO_2Me	25	100	N[d]	N[d]	91 (**8b**)	~5	N[d]
3	2-Me-C_6H_4	CO_2Me	25	100	T[e]	N[d]	90 (**8c**)	~5	N[d]
4	4-Cl-C_6H_4	CO_2Me	15	100	N[d]	N[d]	95 (**8d**)	T[e]	N[d]
5	4-MeO-C_6H_4	CO_2Me	20	100	N[d]	N[d]	92 (**8e**)	T[e]	~5
6	2-Me-C_6H_4	CO_2Et	25	100	T[e]	N[d]	90 (**8f**)	~5	N[d]
7	2-Cl-C_6H_4	CO_2Et	25	100	T[e]	N[d]	91 (**8g**)	~5	N[d]
8	4-Cl-C_6H_4	CO_2Et	15	100	N[d]	N[d]	96 (**8h**)	N[d]	N[d]
9	4-NO_2-C_6H_4	CO_2Et	15	100	N[d]	N[d]	95 (**8i**)	T[e]	N[d]
10	4-MeO-C_6H_4	CO_2Et	20	100	N[d]	N[d]	94 (**8j**)	T[e]	~4

[a] Reaction scale: 3 mmol.
[b] Conversion calculated based on consume of dimedone (TLC).
[c] Isolated yield.
[d] No detected of the this product based on TLC analysis.
[e] Trace yield based on TLC analysis.

In addition to the total overall catalytic activity, recyclability is obviously a critical feature of supported catalysts. As comparison with catalytic efficiency of SBA-15/SO_3H, SiO_2/OSO_3H and $HClO_4$/SiO_2 as the most relevant solid acid have been also investigated in the reaction condition. Employing SBA-15/SO_3H in which the ultrasonic was used, we found that the material displayed minimal loss of activity after 6 runs (Fig. 6).

It is noteworthy that α-aminophosphonate derivatives manifest a number of important and therapeutically useful biologicalactivities [13]. α-aminophosphonates have received significant attention in organic synthesis, and various methods have been developed for their synthesis [14]. Here, we explored the effectiveness of combined ultrasound/nanoreactor catalytically system as an ultra-fast, waste-free and highly reusable method for the generation of α-aminophosphonates **11** via a three-component coupling (Table 5).

The catalytic activity of the simultaneously application of SBA-15/SO_3H nanoreactor and ultrasonic irradiation as a combined catalytic system for three-component synthesis of α-aminophosphonates was studied. The reaction was set under the above optimized conditions at room temperature in EtOH medium (Table 5).

The possibility of recycling the catalyst was then examined. As a model reaction (**11a**), p-chlorobenzaldehyde, aniline and dimethyl phosphite were sonicated in the presence of 2 mol% SBA-15/SO_3H. In this case, after completion of the reactions, the catalyst was filtered and reused at least 7 times without any significant decrease in catalytic activity (Fig. 7).

The synthesis of **11a** with high-scale (20 mmol) amount of reactant was carried out in 25 mL EtOH (Fig. 8). When the *p*-chlorobenzaldehyde and aniline coupled with dimethylphosphite

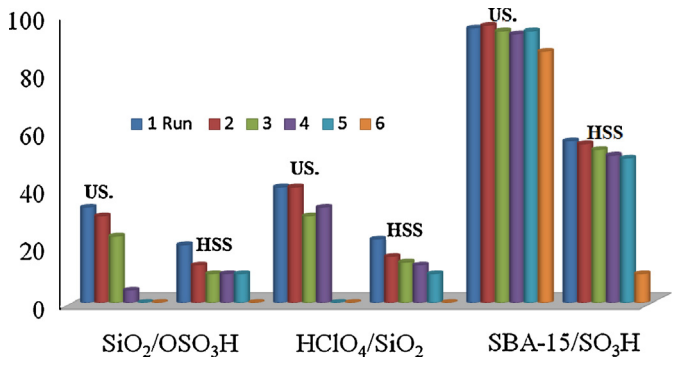


Fig. 6. Recyclability study on the synthesis of **8a**.

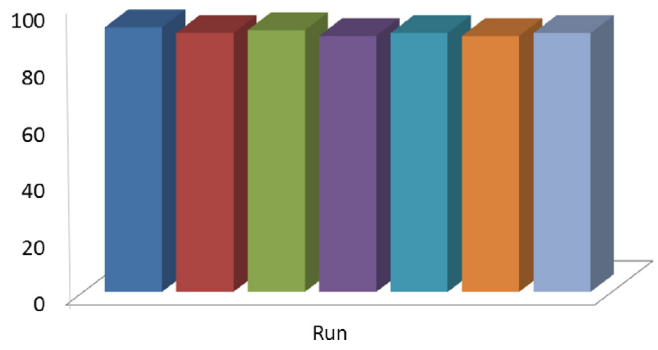
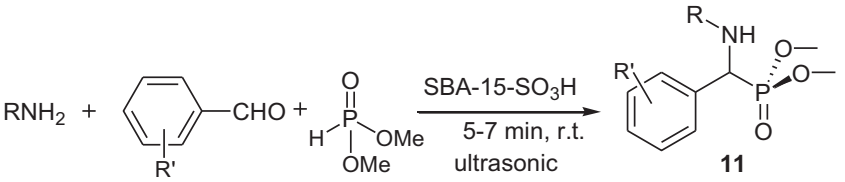


Fig. 7. Recyclability study on the synthesis of **11a**.

Table 5
A ultra-fast waste-free synthesis of α-aminophosphonates 11.[a]



Entry	Amine	Ar(R′)CHO	Time (min)	Yield%[b] **11**
1	$PhNH_2$	4-Cl-C_6H_4	5	94 (**a**)
2	$PhNH_2$	C_6H_5	5	95 (**b**)
3	$PhNH_2$	3-NO_2-C_6H_4	5	95 (**c**)
4	4-Me-$C_6H_4NH_2$	2-Cl-C_6H_4	5	94 (**d**)
5	4-Me-$C_6H_4NH_2$	4-NO_2-C_6H_4	4	95 (**e**)
6	4-Me-$C_6H_4NH_2$	2-MeO-C_6H_4	5	94 (**f**)
7	Et_2NH	3-NO_2-C_6H_4	4	93 (**g**)
8	$(CH_2)_4NH$	2-MeO-C_6H_4	5	94 (**h**)
9	$PhNH_2$	$(CH_2)_5NH$	7	91 (**i**)

[a] Reaction scale: 5 mmol.
[b] Isolated yield method.

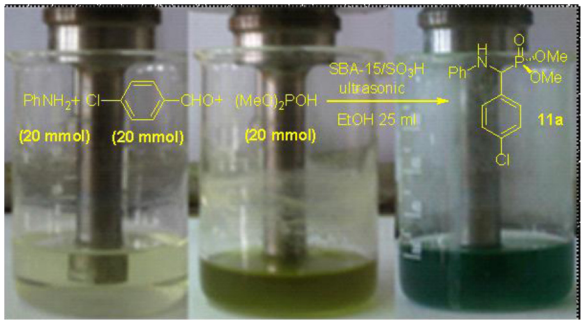


Fig. 8. Progress of reaction in large-scale: (a) beginning of reaction; (b) reaction as it progresses; (c) end of reaction.

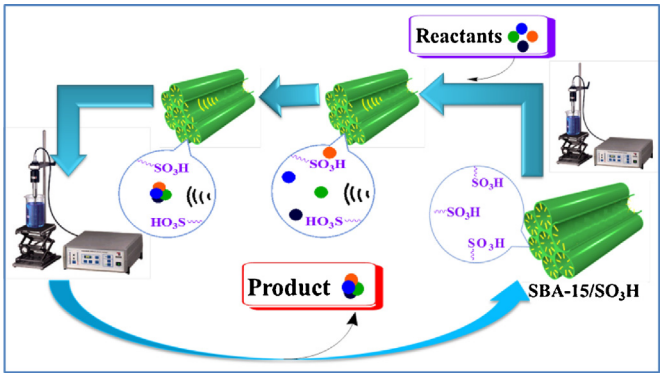
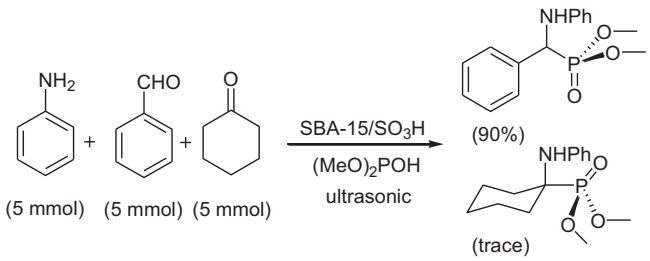


Fig. 9. Possible explanation for SBA-15/SO_3H and ultrasonic irradiation catalysis.

in optimized conditions, a 91% yield was obtained, which showed efficiency of this green method in high-scale amount of substrates.

In a comparative study, the reactivity of dimethyl phosphite in presence of the mixture of aldehydes, ketones with aniline may show the chemoselectivity in our method. To show the chemoselectivity, dimethyl phosphite was treated with the mixture of aniline, benzaldehyde and cyclohexyl ketone. Analysis of the mixture after 10 min shows that only benzaldehyde reacted with aniline to corresponds **11b** (Scheme 3).

Although we have not established the mechanism of the simultaneously application of SBA-15/SO_3H and ultrasonic irradiation in an experimental manner, a possible explanation is proposed in Fig. 9. In this condition the irradiations of ultrasonic in presence of the SBA-15/SO_3H provide a synergistic means to input the reactants and also drive out the products for next recycles.



Scheme 3. Chemoselective addition of phosphite to different carbonyl.

4. Conclusion

Simultaneously application of the ultrasonic and nanoreactor as combined catalytic system in preparation of the some biologically interesting organic molecules via multicomponent reaction. In fact, we have developed a green synthetic method for ultrafast and waste-free preparation of the indazolophthalazinetrione, polyhydroquinolines, and α-aminophosphonate molecules using SO_3H-functionalized SBA-15 porous nanoreactor in presence of an ultrasound. Undoubtedly, as part of the continuing exploration of ultrasonic/nanoreactor for the green organic synthesis, these reaction methods have great prospects of applications in organic syntheses, pharmacy and industrial processes that which this report opens an important field to the use of green strategy in organic process. At the outset of our studies, there was few literature precedent for the direct application of nanoreactor in combination with ultrasound.

Acknowledgements

The author gratefully acknowledges financial support from the Iran National Science Foundation (INSF).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.03.017.

References

[1] (a) P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University, Oxford, 19981–30;
(b) D. Choudhary, S. Paul, R. Gupta, J.H. Clark, Green Chem. 8 (2006) 479;
(c) W.M. V-Rhijn, D.D. Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, Chem. Commun. (1998) 317–318.

[2] (a) K. Tanaka, F. Toda, Chem. Rev. 100 (2000) 1025–1074;
(b) Y. Nishina, K. Takami, Green Chem. 14 (2012) 2380–2383;
(c) Z.-L. Shen, H.-L. Cheong, Y.-C. Lai, W.-Y. Loo, T.-P. Loh, Green Chem. 14 (2012) 2626–2630.

[3] (a) A.H. Latham, M.E. Williams, Acc. Chem. Res. 41 (2008) 411–420;
(b) B.R. Vaddula, A. Saha, J. Leazer, R.S. Varma, Green Chem. 14 (2012) 2133–2336;
(c) D. Strubing, H. Neumann, S. Klaus, S. Hubner, M. Beller, Tetrahedron 61 (2005) 11333–11344.

[4] (a) J. Liu, Q. Yang, M.P. Kapoor, N. Setoyama, S. Inagaki, J. Yang, L. Zhang, J. Phys. Chem. B 109 (2005) 12250–12256;
(b) Q. Yang, M. Kapoor, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 9694–9695;
(c) M. Kapoor, Q. Yang, Y. Goto, S. Inagaki, Chem. Lett. 32 (2003) 914–915.

[5] (a) Q. Yang, M. Kapoor, N. Shirokura, M. Ohashi, S. Inagaki, J.N. Kondo, K. Domen, J. Mater. Chem. 15 (2005) 666–673;
(b) Q. Yang, M. Kapoora, S. Inagakia, N. Shirokura, J.N. Kondo, K. Domen, J. Mol. Catal A: Chem. 230 (2005) 85–89;
(c) B. Karimi, M. Vafaeezadeh, Chem. Commun. (2012) 3327–3329;
(d) B. Karimi, D. Zareyee, Org. Lett. 10 (2008) 3989–3992.

[6] (a) J. Li, L. Li, T. Li, H. Li, J. Liu, Ultrason. Sonochem. 3 (1996) 141;
(b) Q. Liu, H. Ai, Z. Li, Ultrason. Sonochem. 18 (2011) 477;
(c) M. Nabid, S. Tabatabaei, R. Ghahremanzadeh, A. Bazgir, Ultrason. Sonochem. 17 (2010) 159;
(d) T. Kimura, T. Sakamoto, J.M. Leveque, H. Sohmiya, M. Fujita, S. Ikeda, T. Ando, Ultrason. Sonochem. 3 (1996) 157;
(e) J. Li, X. Liu, W.F. Wang, Ultrason. Sonochem. 16 (2009) 331;
(f) S. Rostamnia, K. Lamei, Synthesis (2011) 3080.

[7] (a) S. Sadjadi, H. Sepehrian, Ultrason. Sonochem. 18 (2011) 480;
(b) M. Chtourou, R. Abdelhédi, M.H. Frikha, M. Trabelsi, Ultrason. Sonochem. 17 (2010) 246;
(c) S. Rostamizadeh, A.M. Amani, G.H. Mahdavinia, H. Gelareh Amiri, Sepehrian, Ultrason. Sonochem. 17 (2010) 306;
(d) J.-Y. He, H.-X. Xin, H. Yan, X.-Q. Song, R.-G. Zhong, Ultrason. Sonochem. 18 (2011) 466;
(e) S. Tangestaninejad, V. Mirkhani, M. Moghadam, I. M-Baltork, E. Shams, H. Salavati, Ultrason. Sonochem. 15 (2008) 438;
(f) T. Chave, S.I. Nikitenko, D. Granier, T. Zemb, Ultrason. Sonochem. 16 (2009) 481.

[8] (a) A. Khalafi-Nezhad, F. Panahi, Green Chem. 13 (2011) 2408;
(b) Z. Marková, K. Šišková, J. Filip, K. Šafářová, R. Prucek, A. Panáček, M. Kolář, R. Zbořil, Green Chem. 14 (2012) 2550;
(c) A.H. Lu, E.L. Salabas, F. Schuth, Angew. Chem. Int. Ed. 46 (2007) 1222;
(d) Y. Gao, C.S. Kumar, Biofunctionalization of Magnetic Nanoparticles Biofunctionalization of Nanomaterials, Wiley-VCH, Winheim, 200572;
(e) G.A. Somorjai, J.Y. Park, Angew. Chem. Int. Ed. 47 (2008) 9212.

[9] (a) S. Rostamnia, A. Alizadeh, L.G. Zhu, J. Comb. Chem. 143 (2009) 143;
(b) A. Alizadeh, S. Rostamnia, Synthesis (2010) 1543;
(c) S. Rostamnia, Res. J. Chem. Environ. 15 (2011) 89;
(d) A. Alizadeh, S. Rostamnia, A. Esmaili, Synthesis (2007) 709;
(e) A. Alizadeh, Q. Oskueyan, S. Rostamnia, Synthesis (2007) 2637;
(f) A. Alizadeh, N. Zohreh, S. Rostamnia, Tetrahedron 63 (2007) 8083;
(g) S. Rostamnia, Z. Karimi, M. Ghavidel, J. Sulfur Chem. 33 (2012) 313;
(h) S. Rostamnia, K. Lamei, Chin. Chem. Lett. 23 (2012) 930;
(i) S. Rostamnia, A. Zabardasti, J. Fluorine Chem. 144 (2012) 69;
(j) S. Rostamnia, K. Lamei, M. Mohammadquli, M. Sheykhan, A. Heydari, Tetrahedron Lett. 53 (2012) 5257.

[10] (a) F. Al-Assar, K.N. Zelenin, E.E. Lesiovskaya, I.P. Bezhan, B.A. Chahchir, Pharm. Chem. J. 36 (2002) 598;
(b) R.P. Jain, J.C. Vederas, Bioorg. Med. Chem. Lett. 14 (2004) 3655;
(c) R.W. Carling, K.W. Moore, L.J. Street, D. Wild, C. Isted, P.D. Lesson, S. Thomas, D. O'cooner, R.M. Mckernan, K. Quirk, S.M. Cook, J.R. Atach, K.A. Wafford, S.A. Thompson, G.R. Dawson, P. Ferris, J.L. Castro, J. Med. Chem. 47 (2004) 1807.

[11] (a) M. Sayyafi, M. Seyyedhamze, H.R. Khavasi, A. Bazgir, Tetrahedron 64 (2008) 2375;
(b) J.M. Khurana, D. Magoo, Tetrahedron Lett. 50 (2009) 7300;
(c) R. Ghorbani-Vaghei, R. Karimi, Z. Toghraei, M. Amiri, M. Ghavidel, Tetrahedron 67 (2011) 1930;
(d) T.-S. Jin, Ji-S. Zhang, A.-Q. Wang, T.-S. Li, Ultrason. Sonochem. 13 (2006) 220;
(e) A. Ilangovan, S. Malayappasamy, S. Muralidharan, S. Maruthamuthu, Chem. Cent. J. 5 (2011) 81;
(f) H.N. Karade, M. Sathe, M.P. Kaushik, Arkivoc, xiii (2007) 252;
(g) F. Shirini, N. Ghaffari-Khaligh, Dyes. Pigm. 95 (2012) 789;
(h) H. Lu, J. Li, Z. Zhang, Appl. Organomet. Chem. 23 (2009) 165;
(i) S. Kantaveri, R. Bantu, L. Nagarapu, J. Mol. Catal. A: Chem. 269 (2007) 53.

[12] (a) N. Koukabi, E. Kolvari, A. Khazaei, M.A. Zolfigol, B. Shirmardi-Shaghasemi, H.R. Khavasi, Chem. Commun. 47 (2011) 9230;
(b) F. Tamaddon, Z. Razmi, A.A. Jafari, Tetrahedron Lett. 51 (2010) 1187;
(c) M. Hong, C. Cai, W.-B. Yi, J. Fluorine Chem. 131 (2010) 111;
(d) A. Kumar, R.A. Maurya, Tetrahedron Lett. 48 (2007) 3887;
(e) A. Heydari, S. Khaksar, M. Tajbakhsh, H.R. Bijanzadeh, J. Fluorine Chem. 130 (2009) 609;
(f) S. Khaksar, N. Behzadi, Chin. J. Catal. 33 (2012) 982;
(g) S.M. Baghbanian, S. Khaksar, S.M. Vahdat, M. Farhang, M. Tajbakhsh, Chin. Chem. Lett. 21 (2010) 563.

[13] (a) M.C. Allen, W. Fuhrer, B. Tuck, R. Wade, J.M. Wood, J. Med. Chem. 32 (1989) 1652;
(b) P.P. Giannousis, P.A. Bartlett, J. Med. Chem. 30 (1987) 1603.

[14] (a) B.S. Reddy, A.S. Krishna, A.V. Ganesh, G.G. Kumar, Tetrahedron Lett. 52 (2011) 1359;
(b) A. Heydari, A. Karimian, J. Ipaktschi, Tetrahedron Lett. 39 (1998) 6729;
(c) B.C. Ranu, A. Hajra, U. Jana, Org. Lett. 1 (1999) 1141;
(d) K. Manabe, S. Kobayashi, J. Chem. Soc. Chem. Commun. (2000) 669;
(e) S. Chandrasekhar, S.J. Prakash, V. Jagadeshwar, C. Narsihmulu, Tetrahedron Lett. 42 (2001) 5561;
(f) J.S. Yadav, B.V.S. Reddy, P. Sreedhar, Adv. Synth. Catal. 345 (2003) 564;
(g) A.K. Bhattacharya, T. Kaur, Synlett (2007) 745;
(h) A. Heydari, H. Hamadi, M. Pourayoubi, Catal. Commun. 8 (2007) 1224;
(i) During the preparation of this paper, we noticed that a new interesting sonochemical method based on neat conditions has been reported for α-aminophosphonates (less than 90% yield, and no recycle): B. Dar, A. Singh, A. Sahu, P. Patidar, A. Chakraborty, M. Sharma, B. Singh, Tetrahedron Lett. 53 (2012) 5497;
(j) Also before this hexanesulphonic acid sodium salt as anionic catalyst was used in the ultrasound cleaner condition with a frequency of 40 kHz (output power 250 W, 90 min and no recycle) and 61–97% yield: K.S. Niralwad, B.B. Shingate, M.S. Shingare, Ultrason. Sonochem. 17 (2010) 760.