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Revised

Solvent-free multicomponent reactions using the novel *N*-sulfonic acid modified poly(styrene-maleic anhydride) as a solid acid catalyst

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Highlights

► Poly(styrene-*co*-maleic anhydride) was reacted with 4-aminopyridine and used as a polymeric support.

► This support was reacted with chlorosulfonic acid for the preparation of solid acid catalyst.

► A facile methodology for the solvent-free multicomponent reactions for the synthesis of 4*H*-Pyrimido[2,1-b]benzothiazole derivatives, tetrasubstituted imidazoles and benzoxanthenones were successfully reported.

► This catalyst can promote the yields and reaction times and at least, can be loaded without pre-activation and reused over several repeated runs.

Abstract:

A new *N*-sulfonic acid based on the polymer-support as a solid acid catalyst is prepared by the reaction of the modified poly(styrene-*alt*-maleic anhydride) with neat chlorosulfonic acid. 4*H*-Pyrimido[2,1-b]benzothiazole derivatives, tetrasubstituted imidazoles and benzoxanthenones as selected solvent-free multicomponent reactions were successfully synthesized using this catalyst.

These eco-friendly protocols offer several advantages such as green and cost-effective procedures with excellent yield, shorter reaction time, simpler work-up, recovery, and reusability of metal-free solid acid heterogeneous catalyst along with tolerance of a wide range of functional groups.

Keywords: Polymer-supported catalyst, Poly(styrene-co-maleic anhydride), Acid catalyst, Solvent-free multicomponent reaction

1. Introduction

Assembling several molecules into the product in one reaction step is as a result of the convergent character of multi-component reactions (MCRs) which often give excellent chemo- and regioselective products. These simple, atom economy and time-saving methods make that an important procedure in the synthesis of biologically active compounds such as drugs and agricultural chemicals [1,2].

Increasing the importance of heterocyclic compounds in the field of pharmaceuticals and industrial chemicals has increased the development of simple, elegant and facile methodologies for their synthesis. MCRs reactions remain the most efficient synthetic transformation to produce heterocyclic compounds [3, 4].

Using the eco-friendly reusable heterogeneous catalysts such as solid acids instead of conventional, toxic and polluting traditional homogeneous Brönsted and Lewis acid catalysts is currently in much demand. Solid acids have many advantages over liquid acids in organic reaction catalysis such as their efficiency, easy recyclability and recoverability, operational simplicity, non-corrosive and environmental friendly nature. These benefits make them efficient

catalysts in industry and there are more than 100 industrial transformations using over 103 solid acids at the end of the last century [5-11]. Although, among various supports that can be used for the preparation of the above mentioned catalysts [12-15], silica and zeolite are the more extensively used [16-21], 'leaching' in these supported catalysts leads to loss of activity and they are also thermally unstable above 120 °C in their acid form. Consequently, the synthesis of new support like polymers for the preparation of solid acid catalysts that addresses these drawbacks is enviable [22-25].

Poly(styrene-*co*-maleic anhydride) (SMA) as a commercially available copolymer with reactive anhydride groups, which are susceptible to be modified with different nucleophilic reagents, is an attractive candidate support for design of different reagents [26-31] and catalyst [32]. In the course of our studies on the modification and use of heterogeneous solid acid catalyst in organic transformations [33-38], and in continuation of our interest in synthesis of biologically heterocyclic systems via MCR [39-42] herein we attempted the reaction SMA with 4-aminopyridine and discovered the capability of new modified support in synthesis of new *N*-sulfamic acid modified poly(styrene-maleic anhydride) catalyst. In addition, for the development of environmentally benign chemical methods in which heterogeneous recyclable catalysts are used under solvent-free conditions, we examined the efficiency of this heterogonous catalyst in some solvent-free multicomponent reactions.

2. Experimental

2.1. Materials

N,*N*-Dimethylformamide (DMF) and triethylamine (TEA) were distilled and kept in 4 Å molecular sieve before use. The other reagents were not purified before use and were purchased from Aldrich and Merck with high-grade quality (except SMA). SMA used in this study is KARABOND SAM and its general formula is $[(C_8H_8)_{0.6}\ (C_4H_2O_3)_{0.4}]_n$ with Anhydride/imide content = 40%, M_n = 86666 (g/mol), M_w = 182000 and M_w/M_n = 2.1.

2.2. Equipments

The ^{1}H NMR and ^{13}C NMR spectra were recorded by using Bruker Ultrashield 400 and 100 MHz respectively Advance instrument, with DMSO-d_6 used as solvent. Proton resonances are designated as singlet (s), doublet (d), triplet (t) and multiplet (m). FTIR spectra were recorded using KBr disks on FT-IR Bruker Tensor 27 instrument in the 500-4000cm^{-1} region. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), and strong (s). The scanning electron micrographs of the catalyst surface were recorded using Lecia Cambridge S 360 SEM instrument. Thermogravimetric analysis (TGA/DTG) data were recorded on a Setaram instrument (Caluire, France) at a heating rate of 10 °C/min under nitrogen atmosphere. All yields refer to isolated products.

2.3. Catalyst synthesis

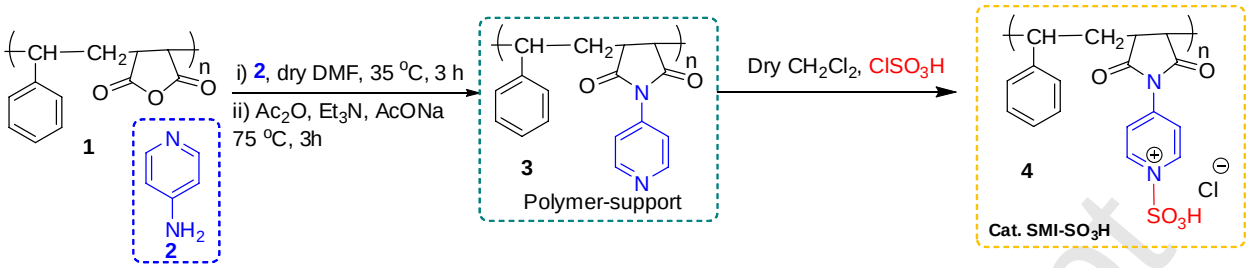
The chemical modification of SMA (**1**) was performed in two steps according to Lee *et al.* optimized reactive condition [43]. 1.00 g SMA, 1.54 g 4-aminopyridine (**2**) and 15 ml dry DMF

were added into a 100-ml glass reactor and then N_2 gas was charged into the reactor and sealed. The reactor was placed into a thermostatic oil-bath on the oscillator and the reactive mixture was oscillated until the reagents dissolved in DMF and kept oscillating at 35 ºC for 3.5 h. After that, 0.6 ml acetic anhydride, 0.33 g sodium acetate and 0.3 ml triethylamine were added into the reactor by syringe (Scheme 1). The temperature was continuously raised to 75 ºC and oscillating for another continued for 3.5 h. The reaction mixture was cooled to room temperature, and was poured slowly into 300 ml of vigorously stirring methanol. A fiber-like precipitated polymer was repeatedly washed with methanol, collected by filtration and dried under reduced pressure at 70 ºC to constant weight. For further purification, the SMI polymer (**3**) was re-precipitated twice.

Chlorosulfonic acid (0.23 mL as a >97% standard solution) was added to a suspension of powdered (0.5 g) SMI in 10 mL dry CH_2Cl_2 over a period of 5 min. The mixture was stirred at room temperature for 6 h then dichloromethane was removed under reduced pressure. The solid powder was dried under vacuum at 65 ºC for 4 h to afford SMI-SO_3H (0.719 g) as a light-yellow powder (Scheme 1).

IR spectrum of SMI (υ_{max}: cm^{-1}): 3209.61 (br), 2928.77 (br), 1783-1705 (s), 1665.01 (s), 1564.80 (s), 1415.83 (s), 1252.92 (w), 1192.59 (w), 1102.29 (w), 763.60 (s).

IR spectrum of SMI-SO_3H (υ_{max}: cm^{-1}): 3208.56 (br), 1721.25 (s), 1655.39 (s), 1531.21 (m), 1288.53 (s), 1175.34 (s), 1069.94 (s), 1007.23 (s), 884.56 (s), 850.87 (s), 578.35 (s).

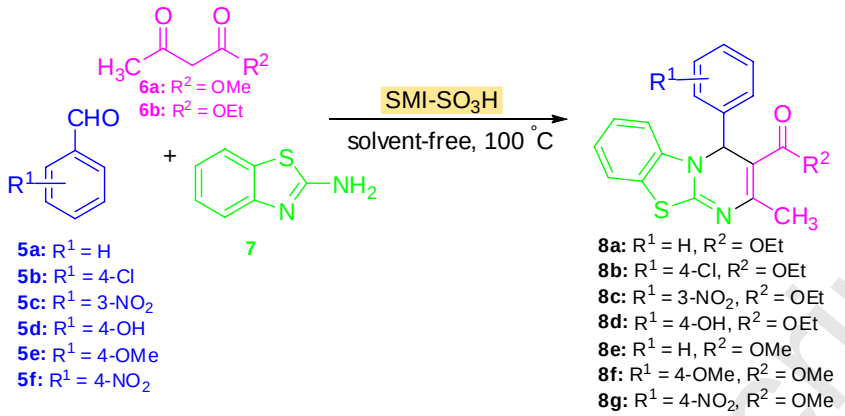


Scheme 1. Preparation of SMI-SO_3H catalyst.

2.4. Catalytic reactions

2.4.1 General procedure for the synthesis of 4*H*-pyrimido[2,1-b]benzothiazole derivatives (8a-g)

A mixture of the ethyl acetoacetate (1 mmol), benzaldehyde (1 mmol), and 2-aminobenzothiazole (1 mmol) in the presence of SMI-SO_3H (0.08g) was stirred at 100 °C in an oil bath. Completion of the reaction was monitored by TLC. After that, the mixture was cooled to room temperature, then hot ethanol was added and the solid heterogeneous catalyst was easily filtrated. The obtained catalyst was washed with acetone and dried under reduced pressured in 70 ºC for 3 h and stored for another consecutive reaction run. The filtrate was concentrated to solidify and the crude product **8a** was purified by re-crystallization from aqueous ethanol in 72% yield. The selected benzothiazole derivatives (**8b-g**) were similarly synthesized and their physical data were determined (Scheme 2).



Scheme 2. Synthesis of 4*H*-pyrimido[2,1-b]benzothiazole derivatives (**8a-g**)

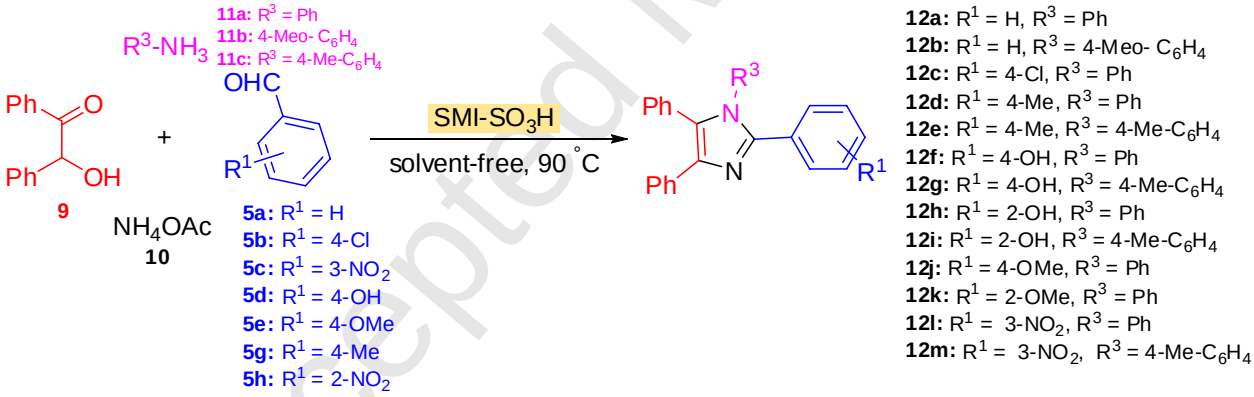
The physical and spectral (melting point (Mp), IR, ^{1}H NMR, and Mass) data for the new derivatives **8b** and **8c** are as follow:

Ethyl-2-methyl-4-(4-chlorophenyl)-4*H*-pyrimido[2,1-b][1,3]benzothiazole-3-carboxylate (8b, $C_{20}H_{17}ClN_2SO_2$): Mp 86-88 °C; IR (υ_{max}, cm^{-1}): 3390, 1699, 1670, 1588, 1496, 744; ^{1}H NMR: δ_H 1.21 (t, 3H, CH_2CH_3), 2.32 (s, 3H, CH_3), 4-4.09 (m, 2H, OCH_2), 6.48 (s, 1H, CH), 7.17-7.20 (t, 1H, ArH), 7.28-7.48 (m, 6H, ArH), 7.73-7.75 (d, 1H, Ar-H) ppm; MS (m/z): 384 (M^+), 355, 311, 273, 245, 199, 175, 134.

Ethyl-2-methyl-4-(3-nitrophenyl)-4*H*-pyrimido[2,1-b][1,3]benzothiazole-3-carboxylate (8c, $C_{20}H_{17}N_3SO_4$): Mp 222-224 °C; IR (υ_{max}, cm^{-1}): 3073,2981, 1656, 1581, 1505, 748; ^{1}H NMR: δ_H 1.21 (t, J = 7 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.99-4.13 (m, 2H, OCH_2), 6.7 (s, 1H, CH), 7.18-8.10 (m, 7H, ArH), 8.36 (s, 1H, ArH) ppm; MS (m/z,%): 395 (M^+), 366, 322, 273, 245, 199, 175, 134.

2.4.2 General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazoles (12a-m)

A mixture of benzil (1 mmol), benzaldehyde (1 mmol), aniline (1 mmol), ammonium acetate (1 mmol) and 0.03 g of SMI-SO_3H was stirred in an oil-bath (90 ºC). After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature. The reaction mixture was soluble in warm absolute ethanol and separated from the catalyst which was insoluble in Ethanol. The recovered catalyst was washed with acetone and dried under reduced pressured in 70 ºC for 3 h and stored for another consecutive reaction run. The pure product **12a** was obtained by re-crystallization of the reaction mixture from ethanol (85% yield). By the application of this reaction condition, other imidazole derivatives (**12b-m**) were synthesized and their physical data were determined (Scheme 3).

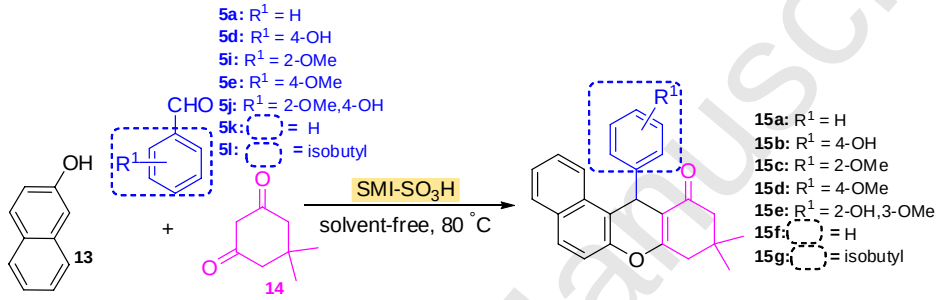


Scheme 3. Synthesis of imidazoles derivatives (**12a-m**)

2.4.3 General procedure for the synthesis of benzoxanthenones (15a-g)

A heterogeneous mixture of β-naphthol (1.0 mmol), benzaldehyde (1.0 mmol), dimedone (1.0 mmol) and SMI-SO_3H (0.07 g) is heated at 80 ºC in an oil bath under solvent-free condition. The progress of the reaction was monitored by TLC. After the completion of the reaction, the product

was extracted with hot ethanol and the catalyst was easily filtered. The filtered catalyst is washed with acetone, dried under reduced pressure, and reused for successive runs. The filtrate is concentrated and the crude product **15a** is re-crystalized from ethanol to give 78% yield. Some selected benzoxanthenones (**15b-g**) were prepared in the similar way and their physical data were compared with those of authentic samples (Scheme 4).



Scheme 4. Synthesis of benzoxanthenones derivatives (**15a-g**)

3. Results and discussion

3.1. Preparation and characterization of the SMI-SO_3H catalyst

The high concentration and reactivity of the cyclic anhydride groups of SMA make this polymer as an ideal support in organic synthesis [26-31]. In continuation of Nàjera and co-workers achievements in using the modified SMA polymer for the synthesis of recoverable palladium catalyst [32], we tried to examine the modification of SMA with 4-aminopyridine as a simpler amine and investigated its ability as a support for the synthesis of solid acid catalysts. The modification of SMA (**1**) with 4-aminopyridine (**2**) was successfully performed in two steps following Lee *et al.* condition [43]. The conversion of maleic anhydride moiety in SMA to maleimide was monitored by FT-IR spectrometer. After the reaction of SMA with 4-aminopyridine, imide peaks were appeared at 1705-1738 cm^{-1} and no peak was observed at

3300-3500 cm^{-1} for amino groups. That is to say, the imidization of SMA was completed and no residual 4-aminopyridine was observed in the resulting SMI. Moreover, the ^1H NMR spectrum of this SMI has been attempted for emphasizing to absolute value of conversion and showed a pattern similar to SMA [43] but aromatic protons of pyridine of residual 4-aminopyridine are observed. In the ^1H NMR spectra of this polymer, appearance of symmetric pseudoquartet C-H proton of pyridine group around 7.99 ppm and absence of N-H peaks of amino group in 4-aminopyridine group indicates the presence of amide groups in the polymer side chain.

IR spectrum of SMI (υ_{max}, cm^{-1}): 3209.61 (s), 2928.77 (s), 1783-1705 (s), 1665.01 (s), 1564.80 (s), 1415.83 (s), 1252.92 (w), 1192.59 (w), 1102.29 (w), 763.60 (s).

^1H NMR of SMI (υ_{max}, cm^{-1}): 1.10 (m, 2H), 1.90 (s, 1H), 2.60 (s, 1H), 2.90 (m, 1H), 6.59 (1H, Ar-H), 6.88 (1H, Ar-H), 6.88-7.36 (5H, Ar-H), 7.99 (2H, Ar-H).

The SMI prepared support was treated with neat chlorosulfonic acid at room temperature under a facile and clean reaction conditions, thus the reaction needed no special work-up (Scheme 1). FTIR spectrum of catalyst is completely different with that of SMI. This may be attributed to the presence of an extra sulfonic acid group on the pyridine nitrogen of SMI-SO_3H which caused the increasing of the number of vibrational in FTIR spectrum of catalyst [22, 44]. The broad band that centered at 3208.56 cm^{-1} in SMI-SO_3H can be assigned to OH stretching of the SO_3H group. In addition, bands at 1288.53, 1175.34, 1069.94, 884.56 and 850.87 cm^{-1} are assigned to the asymmetric and symmetric SO_2 stretching, S-OH bending and symmetric S-N stretching vibrations, respectively in SMI-SO_3H spectrum [45]. On the other hand, "some changes in aromatic ring" as a consequence of the sulfonated pyridine ion formation by the sulfonation reaction, were observed. The bands at 1564.80 and 1415.83 cm^{-1} in SMI spectrum are completely

changed and converted to weaker bands at 1531.21 and 1453.78 cm^{-1} in catalyst spectrum which is related to the sulfonated pyridine ion ring.

IR spectrum of SMI-SO_3H: 3208.56 (br), 1721.25 (s), 1655.39 (s), 1531.21 (m), 1288.53 (m), 1175.34 (s), 1069.94 (s), 1007.23 (s), 884.56 (s), 850.87 (s), 578.35 (s).

As it is clear from the SEM micrographs of SMI and SMI-SO_3H, the primary structure of SMI was completely changed after chemical modifications and the aggregation of particles was retarded in SMI-SO_3H catalyst (Fig. 1a and 1b). Fig. 1c with magnifying 21,000, clearly illustrated the pendant sulfonic groups of the catalyst. Consequently, the surface area of the catalyst was increased with size reductions and retardation of aggregation, which increased the catalytic activity of the catalyst in the organic transformations.

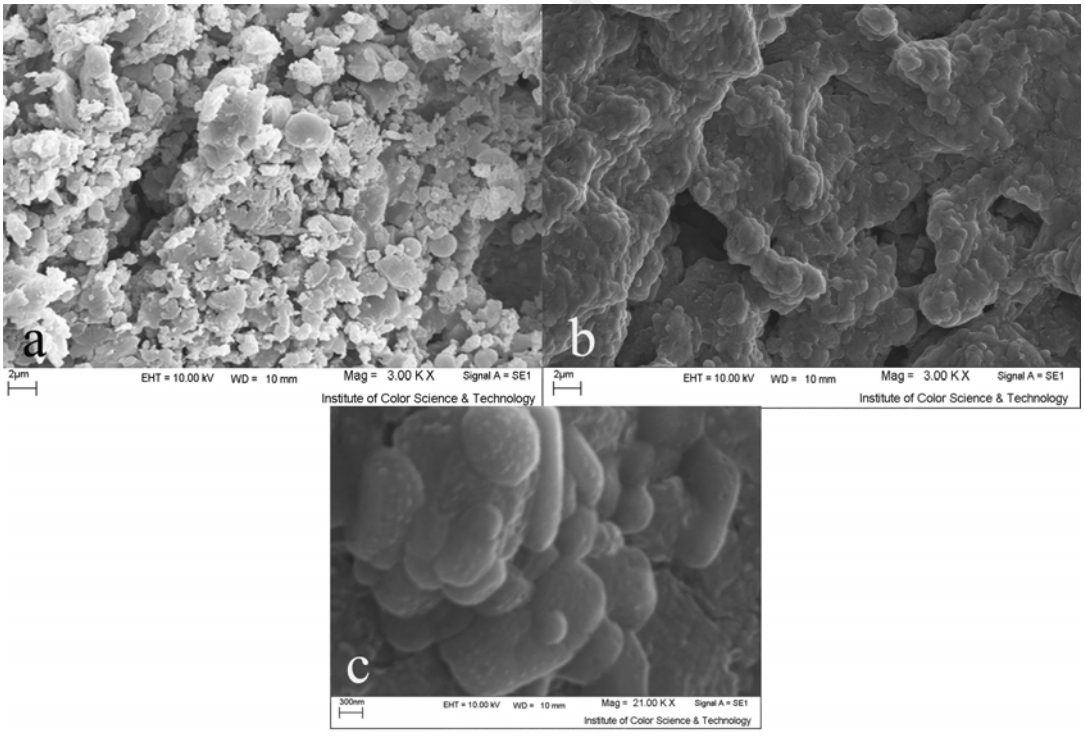


Fig. 1. SEM image of SMI support and SMI-SO_3H catalyst.

TGA and DTGA (differential thermogravimetry) curves of SMI and SMI-SO_3H catalyst under nitrogen were illustrated in Fig 2. and Fig 3., and were used to study the thermal stability of the acid catalyst. A weight loss below 100 ºC in TGA curves is corresponding to the loss of the physically adsorbed solvent or trapped water from SMI and SMI-SO_3H. SMI is thermally stable up to 304 ºC, and could be used as a thermally stable support in the synthesis of various organic catalysts. SMI-SO_3H catalyst was mainly degraded by a four-stage process. The first weight loss in the range of 30-110 ºC, with T_{max} = 62, attributed to the loss of moisture contents. Thermal decomposition of the pendant groups of catalyst caused to other weight loss, T_{max} = 223, 272 and 333 ºC. The 48% weight loss of catalyst in T_{max} = 333 ºC can also be attributed to the thermal decomposition of sulfonic groups. High temperature for the decomposition of the catalyst can be explained as intermolecular bonding interactions of the sulfonated SMI moiety in the solid state, leading to the formation of a rigid network structure [22]. Since ,this catalyst is stable up to 226 ºC it could be considered and selected as a suitable and versatile catalyst in organic transformations requires temperature range of 80-140 °C.

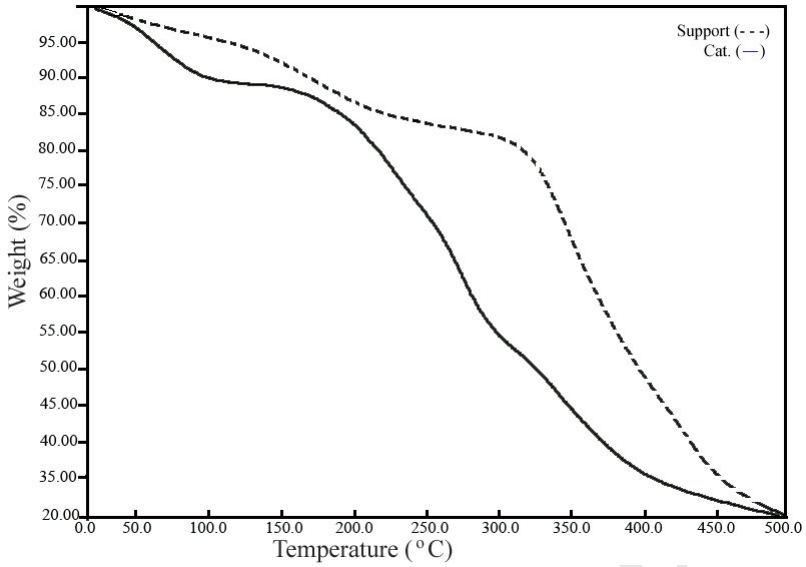


Fig. 2. TGA of SMI support and SMI-SO_3H catalyst.

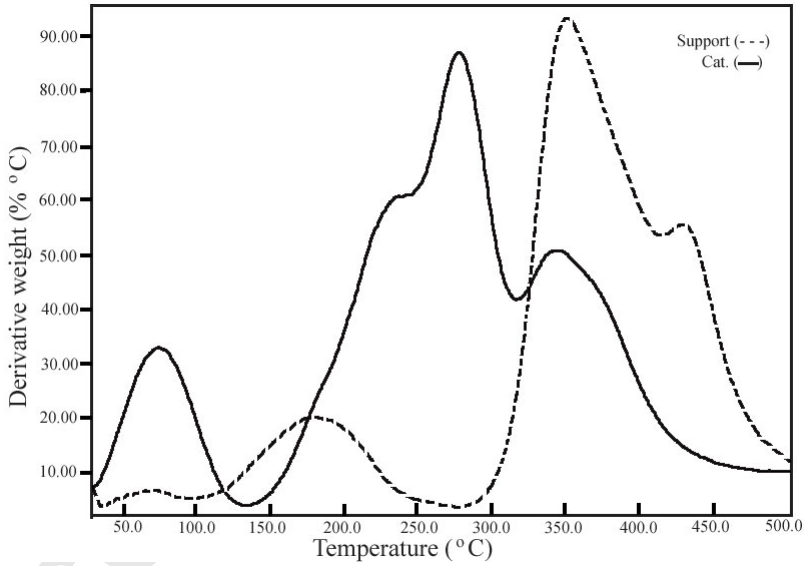


Fig. 3. DTG of SMI support and SMI-SO_3H catalyst.

Anthraquinone (H_0 = -8.2), *p*-nitrotoluene (H_0 = -11.35) and 4-chloronitrobenzene (H_0 = -12.70) were used as Hammett indicators [46] in benzene as the solvent for the evaluation of the acid strength of SMI-SO_3H (Table 1). After evacuating the catalyst at 125 °C for 2 h, it was cooled to room temperature and allowed to contact with the vapor of the Hammett indicator. For

determination of acid contents of SMI-SO_3H through acid-base titration, a standard solution of NaOH was added to a suspension of the catalyst in H_2O-EtOH (1:1). The resulting mixture was stirred for 2 h, and then a 0.01% solution of phenolphthalein in EtOH was added to the suspension as an indicator [22]. The solution was titrated with a standard HCl solution and the acid loading of SMI-SO_3H was found to be in the range of 1.7 and 1.9 mmol g^{-1} by several parallel experiments.

Table 1
Acid strength of SMI-SO_3H

Catalyst	Indicator and H_0		
	Anthraquinone	***p*-Nitrotoluene**	**4-Chloronitrobenzene**
SMI-SO_3H	-8.2 +	−11.35 ±	−12.70 -

+, color changed clearly; −, color unchanged; ±, color changed unclearly.

3.2. Solvent-free multicomponent reaction using SMI-SO_3H catalyst

The structural determination of SMI-SO_3H encouraged us to try this catalyst in multi-component reactions as part of our current studies on the development of new catalysts for the synthesis of heterocyclic systems [33-38]. We initially investigated the efficiency of the catalyst for the synthesis of 4*H*-pyrimido[2,1-b]benzothiazole derivatives (**8a-g**) by the condensation reaction of 2-aminobenzothiazole (**7**) with substituted benzaldehyde (**5a-f**) and β-dicarbonyl derivatives (**6a** and **6b**) (Scheme 2). For the optimization of the reaction condition, the condensation of benzaldehde (**5a**), ethylacetoacetate (**6b**) and 2-aminobenzothiazole (**7**) as a model reaction was selected. Firstly, we investigated the effectiveness of the catalyst by comparing the reaction in 0.07 g of different catalysts. From the result in Table 2, it is clear that the activity of our new catalyst was similar to the Silica Perchloric Acid as an excellent acidic catalyst [47] and also comparable with commercially available Amberlyst-15 catalyst which has many applications in

organic transformations [48]. In addition, the effect of different solvents on the reaction time and yields of the product was examined (Table 3) and we concluded that solvent-free conditions is the condition of choice. Higher yield of solvent-free condition may be attributed to the higher concentration of the reactants in reaction media ,which often facilitate these reactions to be completed in shorter reaction times along with offering an easier workup [49]. The optimization of the amount of the catalyst and reaction temperature indicated that the best result is achievable in the presence of 0.08 g of catalyst at 100 ºC (Table 4). To evaluate the scope and limitations of this methodology, we extended this optimized condition for the preparation of 4*H*-pyrimido[2,1-*b*]benzothiazole derivatives. The results are illustrated in Table 5. It is noteworthy that the use of this catalyst led to the preparation of different 4*H*-pyrimido[2,1-*b*]benzothiazole derivatives in good yield. The selected benzothiazole derivatives (**8a**, **8d-g**) were known and their physical data were compared with those of authentic samples and found to be identical (Table 5) [50, 51]. In addition, the structure of **8b** and **8c** as new compounds were confirmed from their spectral data included infrared (FT-IR), ^{1}H NMR, and mass spectroscopic analyses. The formation of compound **8a** and **8c** were evident from the appearance of [M^{+}] peak at *m/z* = 384 and 395 respectively in mass spectrum $(ESI)^{+}$ and the appearance of characteristic methine proton as singlet at δ = 6.48 and 6.7 ppm respectively in their ^{1}H NMR spectrum.

Table 2
Solvent-free synthesis of **8a** in presence of different catalysts at 100 °C.[a]

Entry	Catalyst	Time (h)	Yield[b] (%)
1	Silica Perchloric Acid	3	65
2	Al_2O_3/KF	5	40
3	Nano-ZnO	3	40
6	$AlCl_3$-HSO_4	3	50

7	$SMI\text{-}SO_3H$	3	69
8	Dawson	3	53
9	Amberlyst-15	3	71
10	-	5	-

[a] 1 mmol (**5a**), 1 mmol (**6b**) and 1 mmol (**7**) in presence of 0.07 g of catalyst
[b] refers to the isolated yield

Table 3
Synthesis of **8a** in presence of different solvents.[a]

Entry	Solvent	Time (h)	Temperature (°C)	Yield[b] (%)
1	H_2O	3	Reflux	45
2	CH_3CH_2OH	3	Reflux	30
3	CH_3CN	3	Reflux	35
4	DMF	3	Reflux	60
5	-	3	100	69

[a] 1 mmol (**5a**), 1 mmol (**6b**) and 1 mmol (**7**) in presence of 0.07 g of catalyst and 5 mL of solvent
[b] refers to the isolated yield.

Table 4
Synthesis of **8a** in presence of different amount of catalyst and temperature.[a]

Entry	Catalyst (g)	Temperature (°C)	Yield[b] (%)
1	0.06	100	60
2	0.07	100	69
3	0.08	100	72
4	0.09	100	72
5	0.08	60	55
6	0.08	80	63
7	0.08	120	71

[a] 1 mmol (**5a**), 1 mmol (**6b**) and 1 mmol (**7**)
[b] refers to the isolated yield.

Table 5
Synthesis of 4*H*-pyrimido[2,1-b]benzothiazole derivatives (**8a-g**) under optimized conditions.[a]

Entry	Product	Time (h)	Yield[b](%)	Mp (°C)/Lit. Mp[ref]
1	**8a**	3	72	178-180/175-176 [44]
2	**8b**	3	71	86-88

3	**8c**	4	69	222-224
4	**8d**	3	73	210-212/205-207 [45]
5	**8e**	3	74	143-145/144-145 [44]
6	**8f**	4	66	150-153/154-157 [44]
7	**8g**	3	76	78-81/86-88 [44]

[a] 1 mmol (**5**), 1 mmol (**6**) and 1 mmol (**7**) in presence of 0.08 g of catalyst at 100 ºC
[b] refers to the isolated yield.

Encouraged by these results, we were enough confident to examine the catalytic power of SMI-SO3H catalyst in another multi-component reaction. Preliminary optimization of synthesis reaction conditions of 1,2,4,5-tetrasubstituted imidazoles was performed using the pair benzyl (**9**), benzaldehyde (**5a**) and aniline (**11a**). The comparison of two solvents and solvent-free conditions (Table 6) showed that the solvent-free condition was the most suitable for the synthesis of **12a**, and therefore it was used in all subsequent experiments. The amount of the catalyst was also optimized and 0.03 g was selected as the best amount (Table 6). The effect of temperature was studied by carrying out both reactions at different temperatures (60, 80, 90, 100 and 120 ºC). It was also observed (Table 6) that yield depends on temperature and it was increased as the reaction temperature was raised. However from 90, 100 to120 ºC there is no appreciable increase in the yields observed. Thus, in the subsequent studies all reactions were carried out at 90 ºC. The optimal conditions were then applied for the preparation of a series of 1,2,4,5-substituted imidazoles (**12a-m**). The product yields are shown in Table 7.

In summary, using this new catalyst provides an efficient route to access diverse and highly functionalized imidazoles. The selected synthesized imidazole derivatives (**12a-m**) were known and their physical data were compared with those of authentic compounds and found to be identical (Table 6) [52-57].

Table 6
Optimization conditions for the synthesis of **12a** in presence of SMI-SO_3H catalyst.[a]

Entry	Product	Solvent	Catalyst (g)	Temperature (°C)	Time (min)	Yield[b] (%)
1	**12a**	H_2O	0.05	Reflux	30	65
2	**12a**	CH_3CH_2OH	0.05	Reflux	35	60
3	**12a**	CH_3CN	0.05	Reflux	45	60
4	**12a**	-	0.05	100	12	80
5	**12a**	-	0.02	100	20	76
6	**12a**	-	0.03	100	12	80
7	**12a**	-	0.04	100	12	80
7	**12a**	-	0.03	60	15	69
8	**12a**	-	0.03	80	12	78
9	**12a**	-	0.03	90	12	80
10	**12a**	-	0.03	120	12	80

[a] 1 mmol (**9**), 1 mmol (**5a**), 1 mmol (**10**), and 1 mmol (**11a)** in 5 mL of solvent (in solution experiments)
[b] refers to the isolated yield.

Table 7
Synthesis of imidazoles derivatives (**12a-m**) under optimized conditions.[a]

Entry	Product	Time (min)	Yield[b] (%)	Mp (˚C)/Lit. Mp[ref]
1	**12a**	12	80	216-218/216-218 [52]
2	**12b**	10	82	171-173/171-173 [52]
3	**12c**	15	88	148-151/148-151 [52]

5	**12d**	10	79	184-185/183-185 [53]
6	**12e**	10	80	192-193/192-194 [54]
7	**12f**	10	93	287-289/285-286 [54]
8	**12g**	15	90	234-236/233-235 [55]
9	**12h**	15	92	250-252/253-255 [55]
10	**12i**	20	89	227-230/227-230 [54]
11	**12j**	10	76	184-186/183-185 [53]
13	**12k**	10	80	150-152/149-152 [56]
15	**12l**	15	79	>300/308-309 [57]
16	**12m**	20	76	150-151/149-151 [54]

[a] 1 mmol (**9**), 1 mmol (**5a**), 1 mmol (**10**), and 1 mmol (**11a**) in presence of 0.03 g catalyst at 90 ºC.
[b] refers to the isolated yield.

Further, three component reaction of β-naphthol (**13**), benzaldehyde (**5a**), and dimedone (**14**) was investigated to synthesize benzoxanthenone **15a** by using the aforementioned catalyst. After the finding of the suitable amount of the catalyst, and temperature (Table 8) and examining of different solvents the best condition including the solvent free condition, 0.07 g of catalyst, and 80 °C is reported as a condition of choice. Other derivatives of benzoxanthenones (**15a-g**) as an important group of biologically active heterocycles were synthesized through these optimum conditions. It is worthwhile to mention that aliphatic aldehyde, such as formaldehyde and isobutyraldehyde, was successfully applied for the synthesis of benzoxanthenone **15f** and **15g** respectively. The selected benzoxanthenones derivatives (**15a-g**) were known and their physical data were compared with those of authentic compounds and found to be identical (Table 9) [58].

Table 8
Optimization conditions for the synthesis of **15a** in presence of SMI-SO_3H catalyst.[a]

Entry	Product	Solvent	Catalyst (g)	Temperature (°C)	Time (h)	Yield[b] (%)
1	**15a**	H_2O	0.05	Reflux	3	Trace

2	**15a**	CH_3CH_2OH	0.05	Reflux	3	Trace
3	**15a**	CH_3CN	0.05	Reflux	3	45
4	**15a**	-	0.05	100	1.5	62
5	**15a**	-	0.04	100	2	58
6	**15a**	-	0.07	100	0.8	71
7	**15a**	-	0.08	100	0.8	71
8	**15a**		0.09	100	0.8	70
9	**15a**	-	0.07	120	0.8	70
10	**15a**	-	0.07	60	1.4	66
11	**15a**	-	0.07	80	0.8	78

[a] 1 mmol (**13**), 1 mmol (**5a**), and 1 mmol (**14)** in 5 mL of solvent (in solution experiments)
[b] refers to the isolated yield.

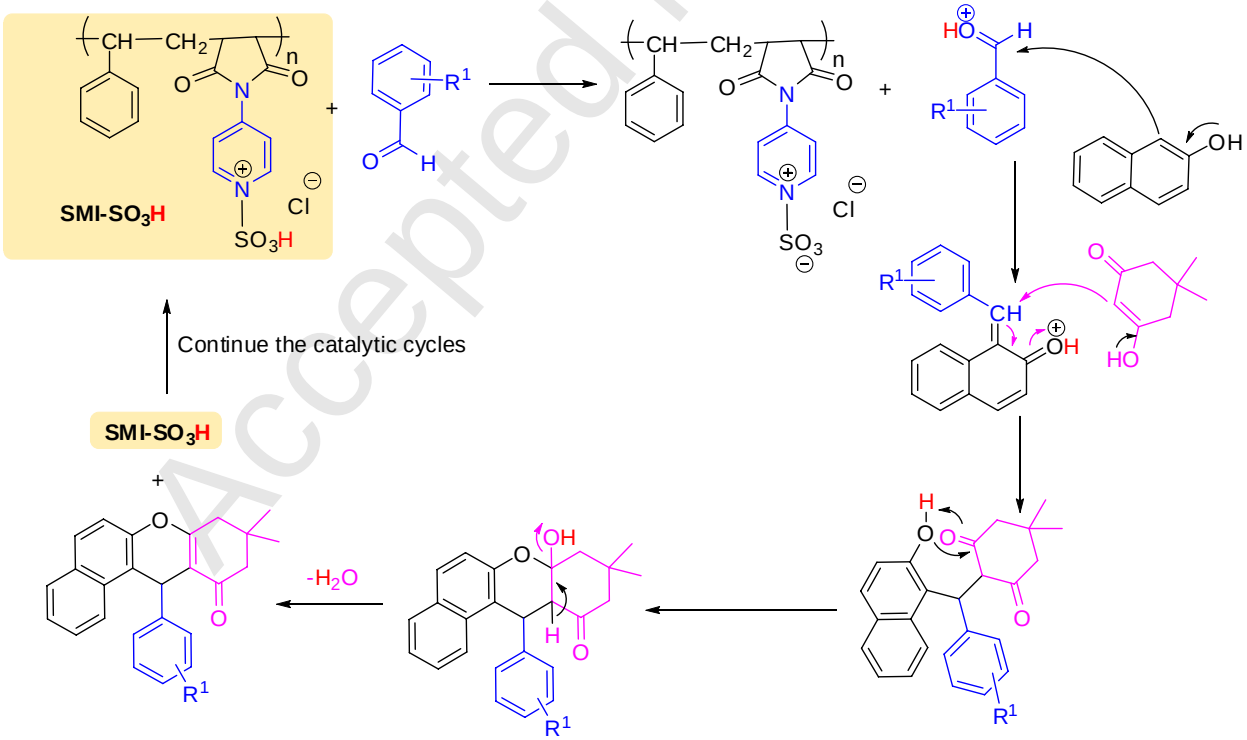
Table 9
Synthesis of benzoxanthenones derivatives (**15a-g**) under optimized conditions.[a]

Entry	Product	Time (h)	Yield[b] (%)	Mp (˚C)/Lit. Mp[ref]
1	**15a**	0.8	78	149-151/152-154 [58]
2	**15b**	0.8	80	220-222/223-224 [58]
3	**15c**	0.75	81	205-208/204-206 [58]
4	**15d**	0.8	80	208-210/203-205 [58]
5	**15e**	0.8	74	181-183/185-187 [58]

6	**15f**	3	66	177-179/173-175 [58]
7	**15g**	3	76	186-189/190-192 [58]

[a] 1 mmol (**13**), 1 mmol (**5a**), and 1 mmol (**14**) in presence of 0.07 g catalyst at 80 ºC.
[b] refers to the isolated yield.

To justify the efficiency of the SMI-SO_3H catalyst in the synthesis of various heterocycles, the possible mechanism for the preparation of benzoxanthenones **15a-g** is proposed (Scheme 5). The reaction proceeds via the ortho-quinone methides intermediate, formed by the nucleophilic addition of 2-naphthol to protonated aldehydes catalyzed by the Brönsted acidic sites of SMI-SO_3H. Subsequent Michael addition of this in situ formed ortho-quinone methides to 1,3-dicarbonyl compound followed by addition of the phenolic hydroxyl moiety to the carbonyl groups of ketone provides cyclic hemiketal which on dehydration affords the product.



Scheme 5. Mechanism of the synthesis of **15a-g**.

From the green chemistry perspective, experiments concerning the recycling and reuse of the catalyst was carried out. Upon completion of the reaction, the catalyst was simply recovered by simple filtration, washing with acetone and drying at 70 ºC for 3 h. The recovered catalyst was then added to a fresh reaction mixture for the synthesis of **8a**, **12a** and **15a** compounds in each selected multi-component reaction. The catalyst could be efficiently recovered and recycled even after 6 cycles without suffering any significant drop in its catalytic activity or the yield of reaction (Fig 4).

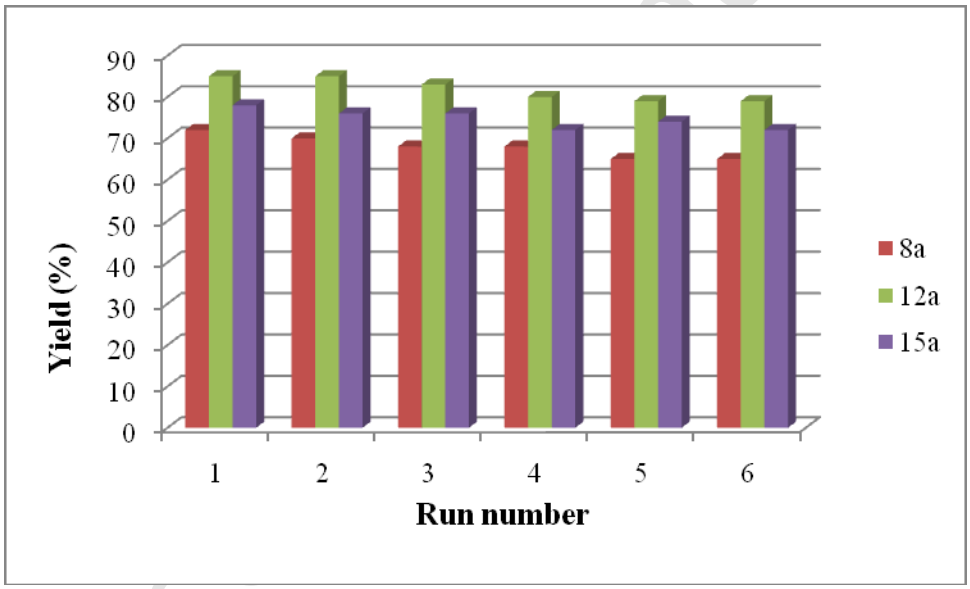


Fig. 4. The recyclability of the SMI-SO_3H in the preparation of **8a**, **12a**, and **15a**.

Conclusions

In summary, the synthesis of novel, thermally stable, green, inexpensive, and easy to prepare solid acid that contain sulfonic acid group, in good yield, is reported. SMI-SO_3H served as an efficient and reusable catalyst in the green synthesis of benzothiazole, 1,2,4,5-tetrasubstituted

imidazole, and benzoxanthenone derivatives. The catalyst plays a crucial role in progress of the reactions in terms of the rate and yield of the products. Also, the use of this catalyst for these transformations avoids the common problems in the recovery of the catalysts. This catalyst system could be easily separated from the reaction mixture with high yields and purity and directly reused after simple extraction. These successful ability of the SMI-SO_3H in the various multi-component reaction may be justified its application in other either known or novel multi-component reactions.

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Figure captions

Scheme 1. Preparation of SMI-SO_3H catalyst.

Scheme 2. Synthesis of 4*H*-pyrimido[2,1-b]benzothiazole derivatives (**8a-g**)

Scheme 3. Synthesis of imidazoles derivatives (**12a-m**)

Scheme 4. Synthesis of benzoxanthenones derivatives (**15a-g**)

Fig. 1. SEM image of SMI support and SMI-SO_3H catalyst.

Fig. 2. TGA of SMI support and SMI-SO_3H catalyst.

Fig. 3. DTG of SMI support and SMI-SO_3H catalyst.

Scheme 5. Mechanism of the synthesis of **15a-g**.

Fig. 4. The recyclability of the SMI-SO_3H in the preparation of **8a**, **12a**, and **15a**.

Table Captions

Table 1. Acid strength of SMI-SO_3H

Table 2. Solvent-free synthesis of **8a** in presence of different catalysts at 100 °C.

Table 3. Synthesis of **8a** in presence of different solvents.

Table 4. Synthesis of **8a** in presence of different amount of catalyst and temperature.

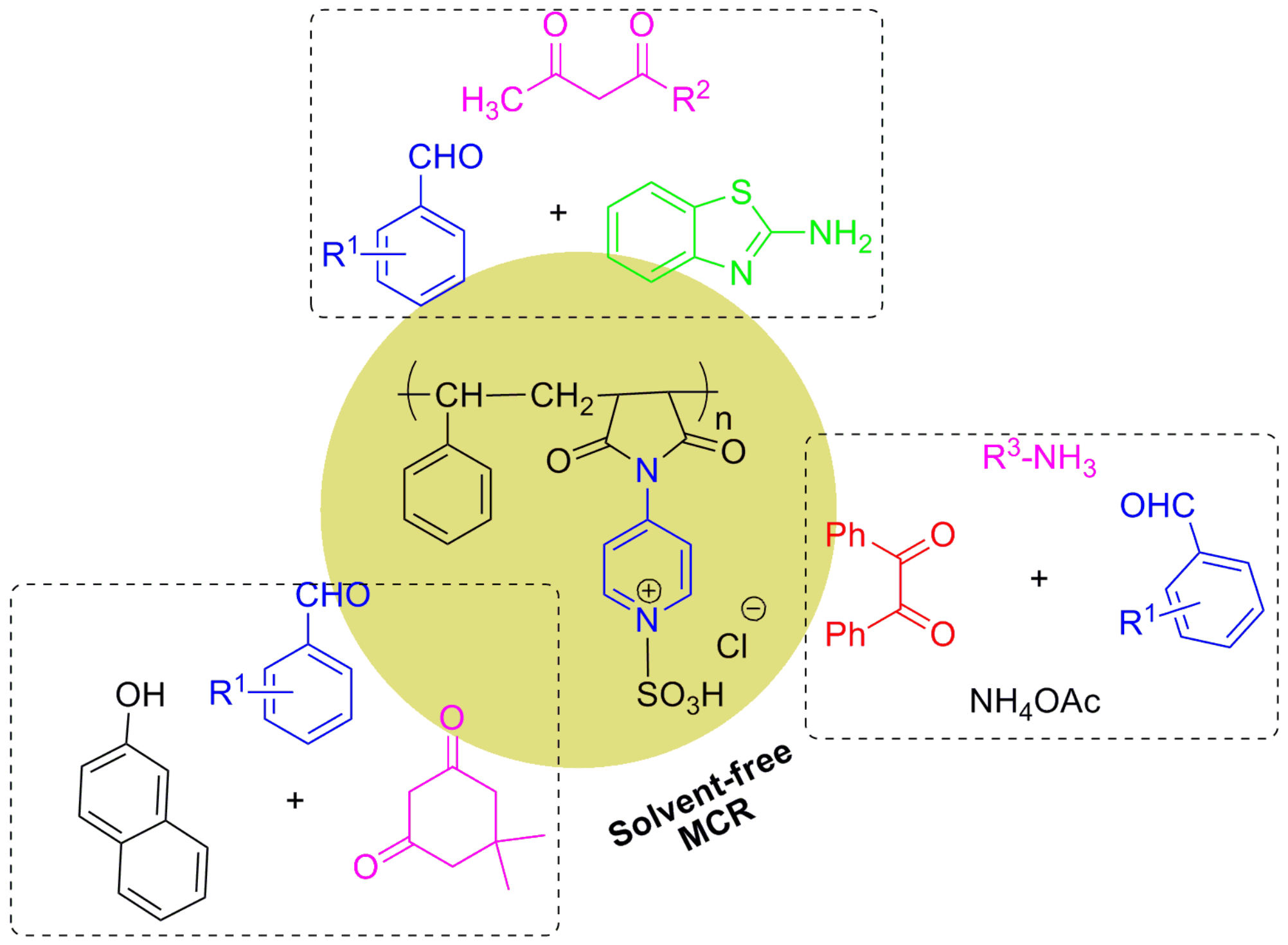
Table 5. Synthesis of 4*H*-pyrimido[2,1-b]benzothiazole derivatives (**8a-g**) under optimized conditions.

Table 6. Optimization conditions for the synthesis of **12a** in presence of SMI-SO_3H catalyst.

Table 7. Synthesis of imidazoles derivatives (**12a-m**) under optimized conditions.

Table 8. Optimization conditions for the synthesis of **15a** in presence of SMI-SO_3H catalyst.

Table 9. Synthesis of benzoxanthenones derivatives (**15a-g**) under optimized conditions.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Solvent-free
MCR