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Facile one-pot synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindoles using sulfonic acid functionalized nanoporous silica (SBA-Pr-SO_3H)

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Sulfonic acid functionalized SBA-15 nanoporous material (SBA-Pr-SO_3H) with a pore size of 6 nm was applied as a new and efficient heterogeneous solid acid catalyst in the one-pot, three-component synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindoles through the reaction of isatins, dimedone, and activated methylene reagents in aqueous medium. SBA-Pr-SO_3H was proved to be a recyclable, green, and highly effective solid acid catalyst which could be easily handled, recovered, and reused several times without significant loss of reactivity. The advantages of this methodology are high product yields, being environmentally benign, short reaction times, and easy handling.

Key words: nanoporous material, SBA-Pr-SO_3H, isatin, spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindoles, green synthesis

INTRODUCTION

The indole nucleus features in a number of natural products which exhibit significant biological activities [1–3]. Furthermore, the spirooxindole ring system is one of the most important spirocycles found in a variety of natural products such as spirotryprostatins A and B [4–6], pteropodine and isopteropodine [7], elacomine and isoelacomine [8, 9], alstonisine [10, 11], strychnofoline [12, 13], horsfiline [14], and coerulescine [15] (Fig. 1). It is also the central structural framework of bioactive molecules [16–19]. Various methodologies were developed for the construction of these heterocyclic skeletons [20–23].

Isatin compound was used extensively in organic synthesis [24, 25]. For example, synthesis of spirooxindoles has been reported by three-component reaction of isatin, dimedone, and activated methylene reagents using different conditions such as MW irradiation [26], sonication [27, 28], electrochemical method [29], in the presence of surfactants [30, 31], using polyethylene glycol (PEG) as the reaction medium [32], and via heating in organic solvents in the presence of tris(2-hydroxyethyl)amine [33], L-proline [34, 35], or lipase [36]. To the best of our knowledge, there have been some reports on the synthesis of spirooxindole derivatives in aqueous medium and a variety of catalysts such as tetrabutylammonium fluoride (TBAF) [37], β-cyclodextrin [38], NH_4Cl [39], ethylenediamine diacetate (EDDA) [40], NEt_3 [41], and tetrabutylammonium bromide (TBAB) [42] have been investigated in refluxing water or heating conditions. However, there is still room for improvement in the present methods so as to overcome the disadvantages of using organic solvents and long reaction times. In this context and in continuation of our studies [43–45], on the

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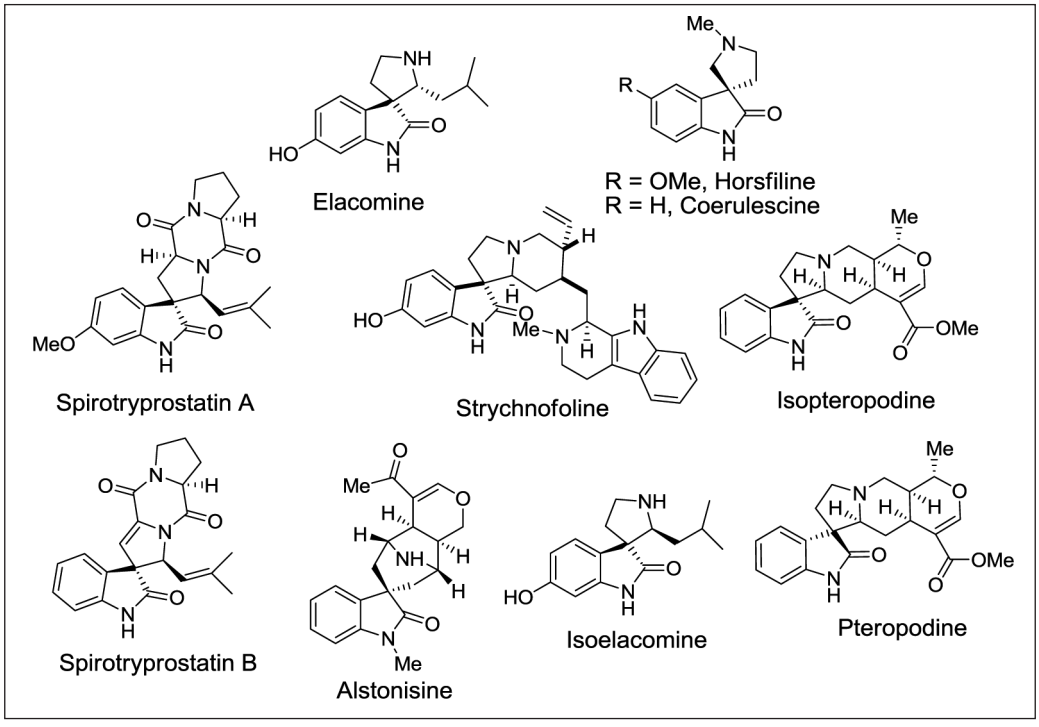


Fig. 1. Representative spirooxindole natural products

application of nanoporous heterogeneous solid acid catalysts in organic synthesis, herein we would like to explore SBA-Pr-SO_3H as a nano-reactor in the green synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindole derivatives in aqueous medium.

SBA-15 having a high surface area, large pore size with narrow pore size distribution and high thermal stability have attracted significant interest in fields ranging from biosensors [46] and drug delivery [47] to separation [48] and catalysis [49]. Loading of organic functional groups while maintaining structural order could be a challenging matter for catalytic applications of SBA-15 [50]. Integration of acidic functional groups (e. g., $-SO_3H$) into SBA-15 has been explored to produce acidic heterogeneous catalysts. Indeed, anchoring of organosulfonic acid on the surface of SBA-15 lets it act as a simple Brønsted acid that donates the protons needed to catalyze the reaction.

RESULTS AND DISCUSSION

In this paper, we want to report a simple, mild and effective method for the one-pot synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindole derivatives via a multicomponent reaction of isatins, dimedone, and activated methylene reagents in the presence of SBA-Pr-SO_3H with a nanopore size about 6 nm which could act as a nano-reactor (Fig. 2).

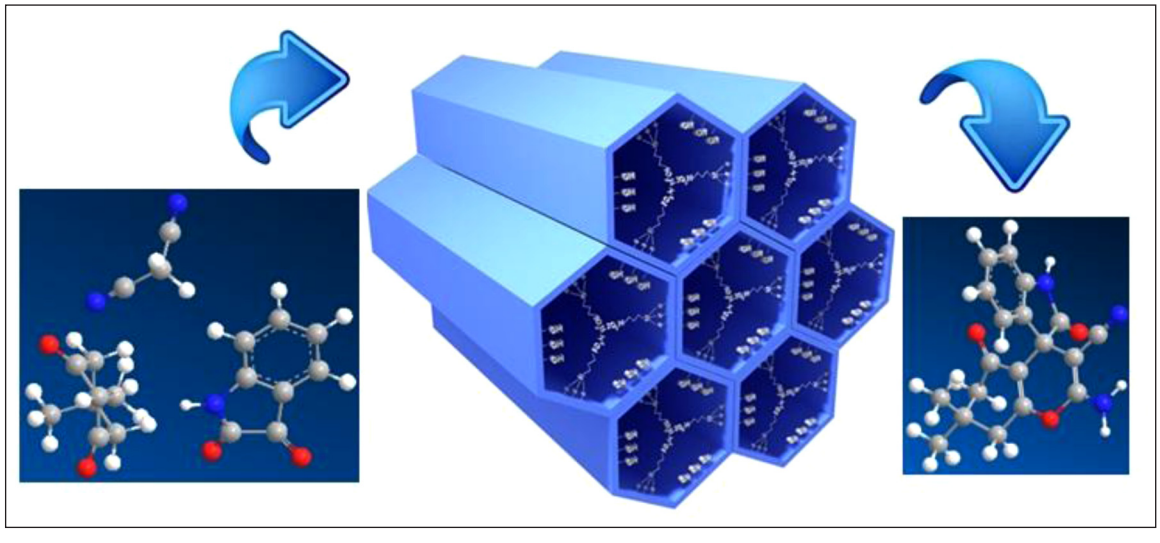


Fig. 2. Synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindole derivatives using SBA-Pr-SO_3H as a nano-reactor

Table 1. **Solvent effects on the synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3′-oxindole 4a**[a]

Entry	Solvent	Time, min	Yield[b], %
1	EtOH	10	80
2	EtOH/H_2O	15	75
3	H_2O	10	90
4	neat (150 °C)	20	80

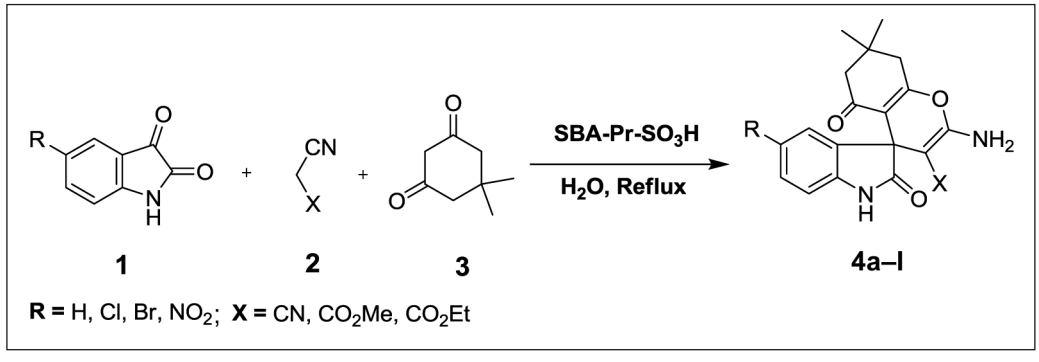
[a] Isatin (2 mmol), dimedone (2 mmol), malononitrile (2 mmol), SBA-Pr-SO_3H (0.02 g).

[b] Isolated yield.

In order to optimize the reaction condition, initially evaluation of various solvent systems was carried out and it was found that the utilization of water as a solvent in the presence of SBA-Pr-SO_3H affords the product **4a** in excellent yield (Table 1). In the absence of any catalyst in water, this reaction afforded compound **4a** after 6 h in very low yield (23%). Then, in regard to library construction, this methodology was evaluated by four types of substituted isatins **1**, malononitrile or cyanoacetic esters **2**, and dimedone **3** in a molar ratio of 1 : 1 : 1 (Scheme 1). Corresponding spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3′-oxindole derivatives were synthesized successfully in good yields in water in the presence of SBA-Pr-SO_3H. The results are summarized in Table 2. As shown by the results in Table 2, when the methylcyano acetate or ethylcyano acetate were used, the reaction time was longer than that of malononitrile, which is probably the result of lower reactivities of the cyanoacetates. After completion of the reaction (monitored by TLC), the crude product was dissolved in hot acetonitrile or methanol, and the catalyst was removed by simple filtration. The acid catalyst can be reactivated by simple washing subsequently with diluted acid solution, water and acetone, and then reused without noticeable loss of reactivity. Some of synthesized derivatives were characterized by M. p., IR, EI-MS, ^{1}H- and ^{13}C-NMR spectral data. Melting points of known products are compared with reported values in the literature as shown in Table 2.

Table 3 illustrates a comparison of the effectiveness of various catalysts used in the synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3′-oxindoles.

The most probable mechanism for this reaction is shown in Scheme 2. Initially, the solid acid catalyst protonates the



Scheme 1. Synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3′-oxindoles **4a-l** in the presence of SBA-Pr-SO_3H

Table 2. **SBA-Pr-SO_3H catalyzed synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3′-oxindoles 4a-l in aqueous media**

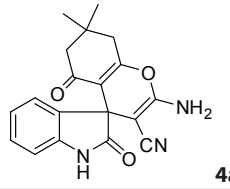
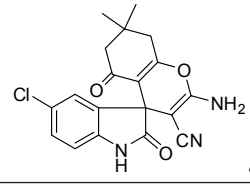
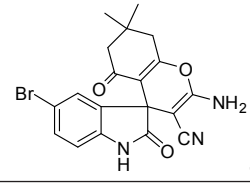
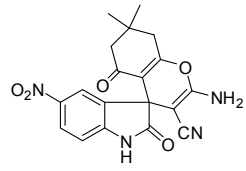
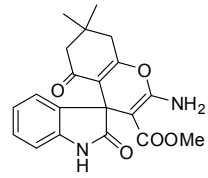
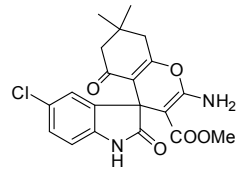
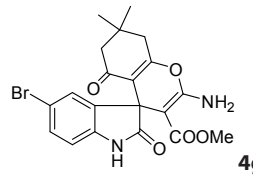
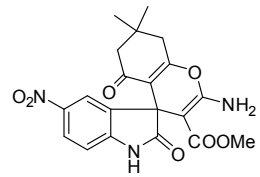
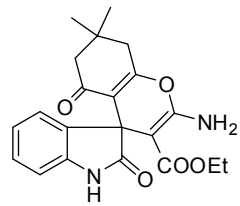
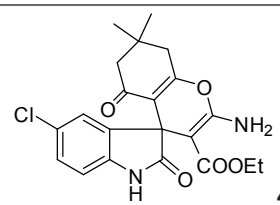
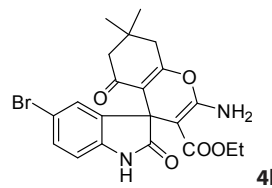
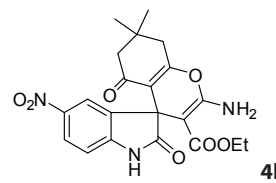
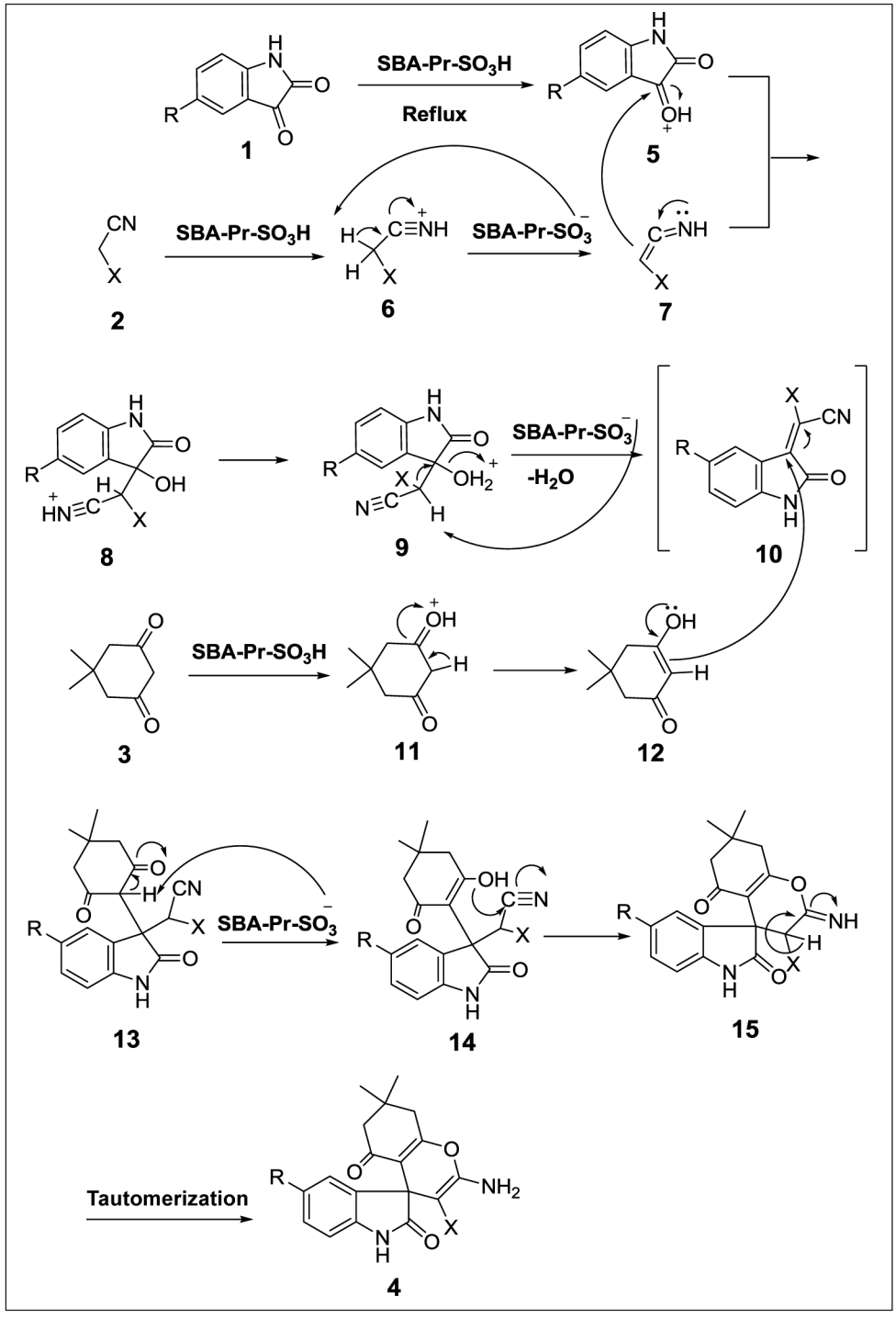
Entry	R	X	Product	Time, min	Yield[a], %	Mp, °C	Mp (lit.)
1	H	CN	 **4a**	10	90	>300	>300 [31]
2	Cl	CN	 **4b**	10	85	>300	>300 [35]
3	Br	CN	 **4c**	10	75	>300	305–307 [29]

Table 2. **Continued**

Entry	R	X	Product	Time, min	Yield[a], %	Mp, °C	Mp (lit.)
4	NO_2	CN	 **4d**	10	80	>300	302–304 [32]
5	H	COOMe	 **4e**	13	70	247–248	255–256 [32]
6	Cl	COOMe	 **4f**	20	80	252–253	New
7	Br	COOMe	 **4g**	15	70	260–262	New
8	NO_2	COOMe	 **4h**	17	80	270–271	New
9	H	COOEt	 **4i**	20	90	255–256	257–258 [39]
10	Cl	COOEt	 **4j**	12	80	267–268	271–272 [36]
11	Br	COOEt	 **4k**	15	85	277–278	260–262 [34]
12	NO_2	COOEt	 **4l**	14	85	274–275	276–278 [27]

[a]Yield of isolated products.



Scheme 2. Proposed mechanism for the synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3′-oxindole derivatives **4a-l**

carbonyl group of isatin **1**, which then condenses with CH-acidic group of cyanoacetic ester **2** through a fast Knoevenagel condensation to afford isatilidene malononitrile derivatives **10**. The Michael addition of dimedone enol form **12** to compound **10** creates intermediate **13** which creates compound **14** by the cycloaddition of hydroxyl group to the cyano moiety. Finally, the desired product **4** was produced by the tautomerization of compound **14** (Scheme 2).

The SBA-15 as a new nanoporous silica can be prepared by using a commercially available triblock copolymer Pluronic P126 as a structure directing agent [51]. Integration of acidic functional groups (e. g., $-SO_3H$) into SBA-15 has been explored to produce promising solid acids. The sulfonic acid functionalized SBA-15 was usually synthesized through direct synthesis or post-grafting [52, 53]. A schematic illustration for the preparation of SBA-Pr-SO_3H was shown in Fig. 3. First, the calcined SBA-15 silica was functionalized with (3-mercaptopropyl) trimethoxysilane (MPTS) and then the thiol groups were oxidized to sulfonic acid by hydrogen peroxide. The surface of the catalyst was analyzed by different

Table 3. **Comparison of different conditions in the synthesis of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindoles**[a]

Entry	Catalyst	Solvent	Condition	Time	Yield	Year
1	–	EtOH	Electrolysis	32 min	96	2007 [29]
2	$InCl_3/SiO_2$	–	MW	3 min	93	2007 [26]
3	$InCl_3$	CH_3CN	Reflux	1.5 h	75	2007 [26]
4	TEBA[b]	H_2O	Heating	2 h	94	2007 [30]
5	Tris(2-hydroxyethyl)amine	EtOH	Heating	2 h	95	2008 [33]
6	TBAF[c]	H_2O	Reflux	30 min	97	2008 [37]
7	NEt_3	EtOH	Reflux	30 min	83	2008 [41]
8	NH_4Cl	H_2O	Heating	10 min	92	2009 [39]
9	β-CD[d]	H_2O	Heating	5 h	90	2009 [38]
10	L-proline	EtOH	Stirring at r. t.	7 min	92	2010 [34]
11	L-proline	H_2O	Heating	20 min	94	2010 [35]
12	EDDA[e]	H_2O	Heating	1 h	90	2010 [40]
13	Sodium stearate	H_2O	Heating	3 h	95	2010 [31]
14	–	PEG	Heating	60 min	92	2010 [32]
15	NaCl	H_2O	Sonication	10 min	98	2011 [27]
16	ZnS NPs[f]	H_2O	Sonication	13 min	96	2011 [28]
17	Lipase	EtOH	Heating	3 h	94	2011 [36]
18	TBAB[g]	H_2O	Reflux	30 min	92	2011 [42]
19	TBAB	–	Heating	40 min	90	2011 [42]
20	SBA-Pr-SO_3H	H_2O	Reflux	10 min	90	This work

[a] Reaction conditions: isatin (2 mmol), dimedone (2 mmol), malononitrile (2 mmol).
[b] TEBA = triethylbenzylammonium chloride.
[c] TBAF = tetrabutylammonium fluoride.
[d] β-CD = β-cyclodextrin.
[e] EDDA = ethylenediamine diacetate.
[f] ZnS NPs = ZnS nanoparticles.
[g] TBAB = tetrabutylammonium bromide.

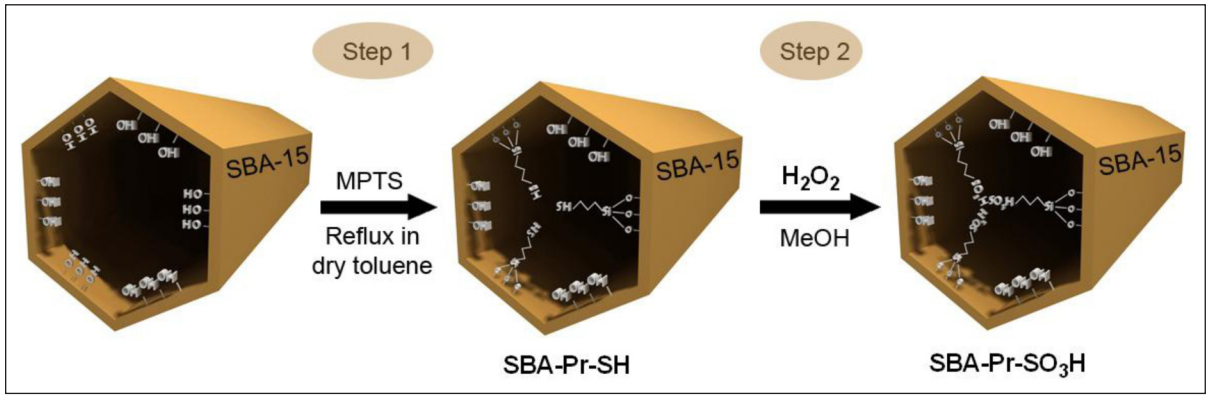


Fig. 3. Schematic illustration for the preparation of SBA-Pr-SO_3H

methods such as TGA, BET and CHN methods which demonstrated that the organic groups (propyl sulfonic acid) were immobilized into the pores [49].

The texture properties of SBA-15 and SBA-Pr-SO_3H are given in Table 4. The surface area, average pore diameter calculated by the BET method and pore volume of SBA-Pr-SO_3H are 440 m^2g^{-1}, 6.0 nm and 0.660 $cm^3\ g^{-1}$, respectively, which are smaller than those of SBA-15 due to the immobilization of sulfonosilane groups into the pores. Fig. 4 illustrates the SEM and TEM images of SBA-Pr-SO_3H. SEM image (Fig. 4 left) shows uniform particles about 1 μm. The same morphology was observed for SBA-15. It can be concluded that morphology of solid was saved without change during the surface modifications. On the other hand, the TEM image (Fig. 4 right) reveals the parallel channels, which resemble the pores configuration of SBA-15. This indicates that the pore of SBA-Pr-SO_3H was not collapsed during two steps reactions.

Table 4. **Porosimetery values for SBA-15 and functionalized SBA-15**

Pore diameter, nm	Pore volume, cm^3g^{-1}	Surface area, cm^2g^{-1}	Catalyst
6.2	0.806	649	SBA-15
6.0	0.660	440	SBA-Pr-SO_3H

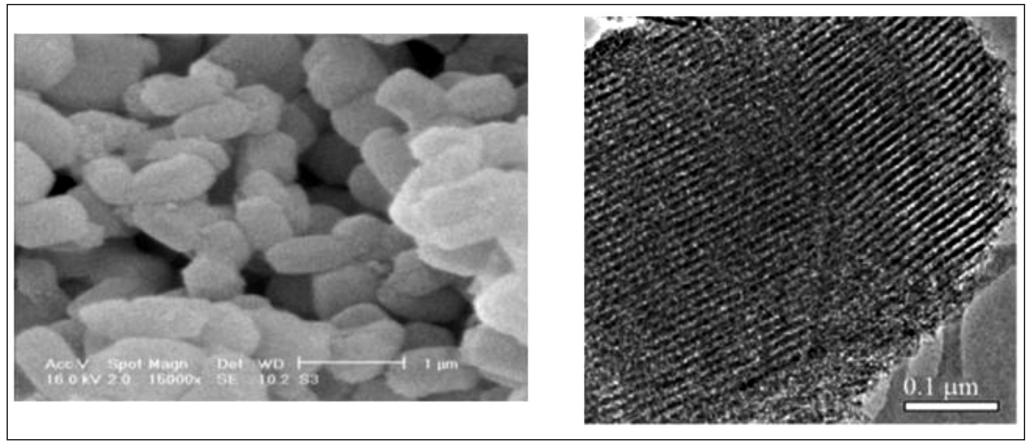


Fig. 4. SEM image (left) and TEM image (right) of SBA-Pr-SO_3H

EXPERIMENTAL

All the reagents and solvents were obtained commercially and used without further purification. IR spectra were recorded from a KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9 200 apparatus. The ^{1}H NMR and ^{13}C NMR were run on a Bruker DPX, in $CDCl_3$ or DMSO-d_6 at 500 and 125 MHz using TMS as the internal standard. GC-Mass analysis was performed on a GC-Mass model: 5973 network mass selective detector, GC 6890 Agilent. SEM analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV while TEM was carried out on a Tecnai G^2 F30 at 300 kV.

SBA-15 nanoporous silica synthesis and functionalization

The nanoporous compound SBA-15 was synthesized and functionalized according to our previous report [49] and the modified SBA-Pr-SO_3H was used as a nanoporous solid acid catalyst in the following reaction.

General procedure for the synthesis of compounds 4a–l

To the reaction mixture containing isatin **1** (2 mmol), malononitrile or cyanoacetic esters **2** (2 mmol), and dimedone **3** (2 mmol) in water (5 ml), SBA-Pr-SO_3H (0.02 g) was added and stirred under reflux conditions as reported time in Table 2. After completion of reaction (TLC monitoring), the generated solid was dissolved in acetonitrile and methanol, filtered for removing the unsolvable catalyst and then the filtrate was cooled to afford the pure products. The catalyst was washed subsequently with diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without loss of significant activity.

Methyl-2-amino-5'-chloro-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carboxylate (4f)

Yield: 80%; mp 252–253 °C; IR (KBr, ν_{max}): 3 330, 3 193, 3 134, 2 956, 2 722, 1 733, 1 597, 1 477, 1 303, 1 247, 1 153, 1 051, 963, 780 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.28 (s, 1H, NH), 7.82 (br. s, 2H, NH_2), 7.05–7.07 (m, 1H, ArH), 6.87 (d, J = 8.0 Hz, 1H, ArH), 6.70 (d, J = 8.2 Hz, 1H, ArH), 3.26 (s, 3H, CH_3), 2.50–2.52 (m, 2H, CH_2), 2.14 (d, J = 15.8 Hz, 1H, CH_AH_B), 2.07 (d, J = 15.8 Hz, 1H, CH_AH_B), 1.04 (s, 3H, CH_3), 0.97 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 195.7 (C=O), 180.4 (C=O, amide), 168.3 (C=O, ester), 163.8, 159.9, 143.7, 138.8, 127.9, 125.3, 123.2, 113.3, 110.2, 76.8, 51.4 (CH_2), 47.8, 40.9, 39.9, 32.4 (CH_2), 28.3 (CH_3), 27.8 (CH_3); EI-MS: 402 (M^+), 343 (100), 318, 304, 260, 83, 55; Anal. calcd. for $C_{20}H_{19}ClN_2O_5$: C, 59.63; H, 4.75; N, 6.95. Found: C, 59.81; H, 4.85; N, 7.15.

Methyl-2-amino-5'-bromo-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carboxylate (4g)

Yield: 70%; mp 260–262 °C; IR (KBr, ν_{max}): 3 337, 3 200, 2 946, 1 695, 1 617, 1 522, 1 475, 1 300, 1 224, 1 186, 1 052, 906, 785 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.29 (s, 1H, NH), 7.85 (br. s, 2H, NH_2), 7.21 (d, J = 7.6 Hz, 1H, ArH), 6.66 (d, J = 8.0 Hz, 1H, ArH), 3.27 (s, 3H, CH_3), 2.49–2.53 (m, 2H, CH_2), 2.15 (d, J = 15.8 Hz, 1H, CH_AH_B), 2.08 (d, J = 15.8 Hz, 1H, CH_AH_B), 1.00 (s, 3H, CH_3), 0.96 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 195.2 (C=O), 180.4 (C=O, amide), 163.8 (C=O, ester), 159.9, 144.1, 138.8, 125.9, 113.3, 110.8, 51.4 (CH_2), 40.9, 39.9, 32.4 (CH_2), 28.3 (CH_3), 27.9 (CH_3); EI-MS: 448 (M^+), 389 (100), 362, 309, 281, 250, 83; Anal. calcd. for $C_{20}H_{19}BrN_2O_5$: C, 53.71; H, 4.28; N, 6.26. Found: C, 53.39; H, 4.55; N, 6.60.

Methyl-2-amino-5'-nitro-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carboxylate (4h)

Yield: 80%; mp 270–271 °C; IR (KBr, ν_{max}): 3 379, 3 189, 2 954, 1 727, 1 685, 1 620, 1 522, 1 445, 1 329, 1 213, 1 090, 1 059, 907, 746 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.95 (s, 1H, NH), 8.14 (br. s, 2H, NH_2), 7.74–7.93 (m, 1H, ArH), 6.91 (d, J = 8.0 Hz, 1H, ArH), 6.89 (d, J = 8.1 Hz, 1H, ArH), 3.32 (s, 3H, CH_3), 2.56 (d, J = 15.8 Hz, 2H, CH_2), 2.12 (d, J = 15.9 Hz,

1H, CH_AH_B), 2.09 (d, J = 15.7 Hz, 1H, CH_AH_B), 1.00 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); EI-MS: 413 (M^+), 354 (100), 329; Anal. calcd. for $C_{20}H_{19}N_3O_7$: C, 58.11; H, 4.63; N, 10.16. Found: C, 57.89; H, 4.29; N, 10.54.

Ethyl-2-amino-5'-chloro-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carboxylate (4j)

Yield: 80%; mp 267–268 °C; IR (KBr, ν_{max}): 3 383, 3 277, 3 214, 2 957, 1 726, 1 687, 1 614, 1 514, 1 476, 1 350, 1 219, 1 169, 1 052, 907, 747 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 10.28 (s, 1H, NH), 7.90 (br. s, 2H, NH_2), 6.67–7.09 (m, 3H, ArH), 3.72 (q, J = 7.3 Hz, 2H, CH_2), 2.49–2.53 (m, 2H, CH_2), 2.14 (d, J = 15.8 Hz, 1H, CH_AH_B), 2.08 (d, J = 15.7 Hz, 1H, CH_AH_B), 1.00 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0.80 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 195.7 (C=O), 180.4 (C=O, amide), 168.3 (C=O, ester), 163.7, 160.0, 144.0, 139.0, 127.8, 125.2, 123.2, 113.3, 110.2, 59.8 (CH_2), 51.4 (CH_2), 40.3, 32.4 (CH_2), 28.3 (CH_3), 27.9 (CH_3), 14.0 (CH_3); EI-MS: 416 (M^+), 343, 153, 83, 55; Anal. calcd. for $C_{21}H_{21}ClN_2O_5$: C, 60.51; H, 5.08; N, 6.72. Found: C, 60.78; H, 5.39; N, 6.91.

Ethyl-2-amino-5'-bromo-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carboxylate (4k)

Yield: 85%; mp 277–278 °C; IR (KBr, ν_{max}): 3 386, 3 276, 3 213, 2 955, 1 726, 1 686, 1 612, 1 512, 1 474, 1 350, 1 216, 1 165, 1 050, 940, 746 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 10.29 (s, 1H, NH), 7.91 (br. s, 2H, NH_2), 6.64–7.22 (m, 3H, ArH), 3.72 (q, J = 6.1 Hz, 2H, CH_2), 2.49–2.53 (m, 2H, CH_2), 2.11 (d, J = 15.7 Hz, 1H, CH_AH_B), 2.09 (d, J = 15.9 Hz, 1H, CH_AH_B), 1.00 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 0.82 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.7 (C=O), 180.2 (C=O, amide), 168.3 (C=O, ester), 163.7, 160.0, 144.4, 139.3, 130.7, 125.9, 113.3, 110.8, 59.8 (CH_2), 51.4 (CH_2), 40.4, 32.4 (CH_2), 28.2 (CH_3), 27.9 (CH_3), 14.0 (CH_3); EI-MS: 460 (M^+), 444, 387 (100), 378; Anal. calcd. for $C_{21}H_{21}BrN_2O_5$: C, 54.68; H, 4.59; N, 6.07. Found: C, 55.01; H, 4.87; N, 6.44.

Ethyl 5'-nitro-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carboxylate (4l)

Yield: 85%; mp 274–275 °C; IR (KBr, ν_{max}): 3 522, 3 367, 3 255, 3 190, 2 958, 1 725, 1 686, 1 621, 1 524, 1 470, 1 332, 1 216, 1 170, 1 058, 907, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 10.04 (s, 1H, NH), 8.08 (s, 2H, NH_2), 6.91–7.71 (m, 3H, ArH), 3.87 (q, J = 6.5 Hz, 2H, CH_2), 2.49–2.53 (m, 2H, CH_2), 2.17 (d, J = 16.1 Hz, 1H, CH_AH_B), 2.08 (d, J = 16.1 Hz, 1H, CH_AH_B), 1.01 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.88 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.7 (C=O), 180.4 (C=O, amide), 163.8 (C=O, ester), 159.5, 150.2, 143.0, 137.0, 125.7, 118.8, 113.4, 108.7, 77.8, 60.4 (CH_2), 51.4 (CH_2), 40.4, 32.3 (CH_2), 28.8, 28.0 (CH_3), 13.7 (CH_3); EI-MS: 427 (M^+), 419, 389, 354, 343, 83, 58; Anal. calcd. for $C_{21}H_{21}N_3O_7$: C, 59.01; H, 4.95; N, 9.83. Found: C, 58.63; H, 4.59; N, 10.20.

CONCLUSIONS

In conclusion, we have developed an efficient and mild procedure for the synthesis of a series of spirocyclic (5,6,7,8-tetrahydro-chromene)-4,3'-oxindole derivatives via the one-pot three-component reaction of corresponding isatin, dimedone, and activated methylene compounds. The use of SBA-Pr-SO_3H in this reaction has the advantages of being a reusable and environmentally benign nano-reactor that the reaction proceeds easily in its nano-pores. Using water as the reaction media is another aspect of green chemistry in this method. High yields, short reaction times, mild reaction condition, and simple workup procedures are further merits of the reported method.

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NESUDĖTINGA VIENOS STADIJOS SPIROCIKLINIŲ (5,6,7,8-TETRAHIDROCHROMENO)-4,3'-OKSINDOLŲ SINTEZĖ NAUDOJANT SULFONINE RŪGŠTIMI FUNKCIONALIZUOTĄ NANOPORINGĄ SILICIO DIOKSIDĄ (SBA-Pr-SO_3H)

S a n t r a u k a

Sulfonine rūgštimi funkcionalizuotas nanoporingas silicio dioksidas, turintis 6 nm dydžio poras, panaudotas heterogeniniu rūgštiniu katalizatoriumi paprastai vienos stadijos trikomponentei spirociklinių (5,6,7,8-tetrahidrochromeno)-4,3'-oksindolų sintezei.