



One-pot solvent-free synthesis of pyranonaphthoquinone-fused spirooxindoles catalyzed by SBA-IL

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KEYWORDS

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 Mesoporous silica;
 Heterogeneous
 catalyst.

Abstract. In this research, ionic liquid modified SBA-15 mesoporous material (SBA-IL) as a recyclable, heterogeneous catalyst efficiently catalyzed the synthesis of pyranonaphthoquinone-fused spirooxindoles through the one-pot three-component reaction of isatin derivatives, activated methylene reagents, and 2-hydroxy-1,4-naphthoquinone. The reactions were performed under microwave irradiation and solvent-free conditions. The synthesized SBA-IL was characterized by SEM, FT-IR, nitrogen adsorption-desorption, and thermogravimetric analyses. Excellent chemical yield, short reaction time, mild reaction condition, easy workup procedures, and reusability of catalyst are noteworthy advantages of this protocol.

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1. Introduction

Since the discovery of a class of periodic mesoporous silica, known as the M41S phase, by the Mobil Oil Company in 1992 [1], mesoporous silica materials have gained considerable attention. SBA-15 materials as a kind of mesoporous silica possess a number of special physical and chemical properties such as well-ordered hexagonal structure, high surface area, and high thermal stability that make them a unique inorganic solid support. Chemical modification of SBA-15 can create a wide variety of novel materials with improved catalytic properties as compared to conventional catalysts [2].

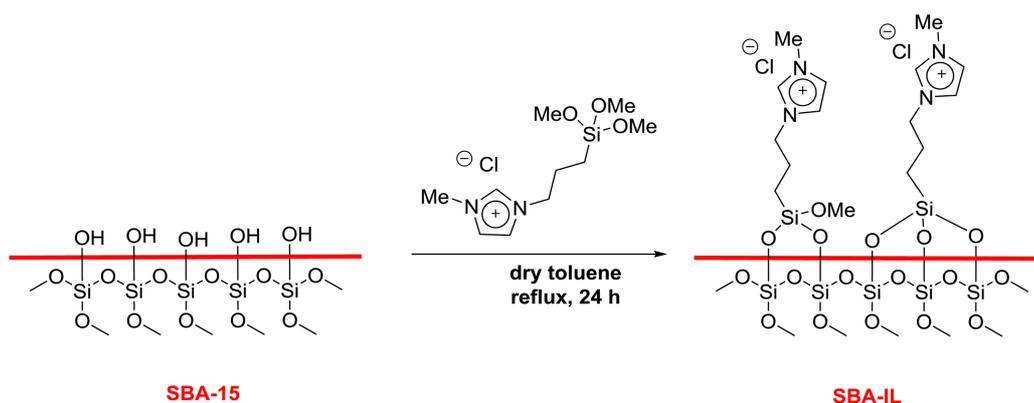
Besides their use as catalysts [3], modified SBA-15 silica materials are considered as a promising class of materials in various areas including chemosensors [4,5], adsorbents [6], gas storage [7], drug delivery [8,9], etc. Among different organically modified SBA-15 materials, immobilization of Ionic Liquids (ILs) onto solid-based materials has received significant attention of researchers. ILs have emerged as promising environmentally benign media, not only as favorable solvents for catalysis but also as green catalysts themselves in various reactions [10]. Although the recovery of involatile IL from reactions is achievable in many cases, liquid-phase processing is still required. The support of ILs on solids to provide heterogeneous systems gave significant improvement in this context, in which simpler workup procedures via filtration/decantation of the solid material were allowed [11].

Heterocyclic compounds have received tremendous attention in the chemical literature as a result of their abundance in natural products and their diverse

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Scheme 1. Preparation of ionic liquid functionalized SBA-15 (SBA-IL).

2.3. General procedure for the synthesis of pyranonaphthoquinone-fused spirooxindoles (4a-h)

2.3.1. Method A: Conventional heating

SBA-IL (0.02 g) was added to a mixture of isatin derivatives (1 mmol), activated methylene reagents (1 mmol), and 2-hydroxynaphthalene-1,4-dione (1 mmol, 0.174 g) under solvent-free conditions. The reaction mixture was stirred at 150°C for an approximate amount of time. The progress of the reaction was monitored by TLC using EtOAc/*n*-hexane (1:2) as the eluent. Upon completion of the reaction, the crude product was dissolved in ethyl acetate. Since SBA-IL was insoluble in ethyl acetate, it was simply separated by filtration. Ethyl acetate was vaporized by heating and the solid pure product was obtained through recrystallization of the filtrate. All products were characterized by comparison of their physical data with those of known compounds reported in the literature. The catalyst was washed subsequently with ethanol, dried under vacuum, and reused several times without significant loss of activity.

2.3.2. Method B: Microwave irradiation

To a solution of isatin derivatives (1 mmol), activated methylene reagents (1 mmol), and 2-hydroxynaphthalene-1,4-dione (1 mmol, 0.174 g), SBA-IL (0.02 g) was added and the mixture was stirred at room temperature. The mixture of the reaction was then irradiated in a domestic microwave oven for 8 min at 800 W. The work-up procedure and characterization of compounds were same as those mentioned before.

2.4. Spectral data of some representative products

2.4.1. 2-Amino-5'-chloro-2',5,10-trioxo-5,10-dihydrospiro[benzo[*g*]chromene-4,3'-indoline]-3-carbonitrile C₂₁H₁₀ClN₃O₄ (4b)

Yellow powder; mp 258-260 (dec); (93% Method A, 90% Method B); FT-IR (KBr), ν (cm⁻¹): 3335, 3250, 3184, 2209, 1743, 1716, 1675, 1340 and 1207. ¹H NMR

(250 MHz, DMSO-*d*₆): δ_H (ppm) 6.87 (1H, d, $J = 8.2$ Hz, ArH), 7.22-8.05 (6H, m, ArH), 7.84 (2H, bs, NH₂), 10.82 (1H, s, NH). ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ_C (ppm) 48.7, 56.7, 111.4, 117.2, 119.1, 124.9, 126.3, 126.4, 126.6, 129.1, 130.7, 130.9, 134.9, 135.2, 136.7, 141.1, 151.1, 159.1, 176.7, 177.7, 182.3.

2.4.2. 2-Amino-5'-iodo-2',5,10-trioxo-5,10-dihydrospiro[benzo[*g*]chromene-4,3'-indoline]-3-carbonitrile C₂₁H₁₀IN₃O₄ (4d)

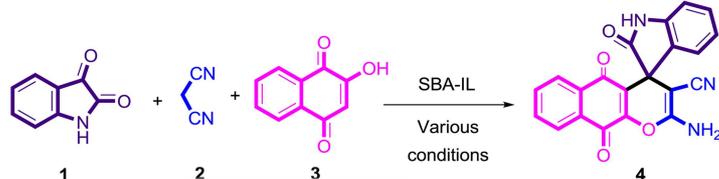
Orange powder; mp 262-263 (dec); (94% Method A, 90% Method B); FT-IR (KBr), ν (cm⁻¹): 3444, 3381, 3159, 2215, 1737, 1667, 1652, 1334 and 1205. ¹H NMR (250 MHz, DMSO-*d*₆): δ_H (ppm) 6.83 (1H, d, $J = 8.2$ Hz, ArH), 7.35-8.54 (8H, *m*, ArH and NH₂), 10.81 (1H, s, NH). ¹³C-NMR (62.5 MHz, DMSO-*d*₆): δ_C (ppm) 56.8, 60.2, 111.9, 114.0, 117.2, 119.1, 126.4, 126.6, 127.6, 130.8, 130.9, 132.0, 134.9, 135.2, 137.1, 141.5, 151.1, 159.1, 176.7, 177.6, 182.3.

3. Results and discussion

3.1. The synthesis of pyranonaphthoquinone-fused spirooxindoles

Due to our interest in application of nanoporous heterogeneous solid catalysts in organic reactions, herein, we report a facile synthesis of pyranonaphthoquinone-fused spirooxindoles **4** from commercially available isatins **1**, malononitrile **2**, and 2-hydroxy-1,4-naphthoquinone **3** catalyzed by nano-ordered SBA-IL. To date, many attempts have been devoted to the development of catalysis with ILs for fine chemical synthesis. In this context, solid catalysis with ILs can be a very promising candidate for developing green processes for the synthesis of various organic compounds [34]. Modification of surface of SBA-15 with imidazolium cations takes advantage of excellent features of both SBA-15 and ionic liquid [35-37].

In order to optimize the condition of reaction, initially, we screened the effect of solvent and temper-

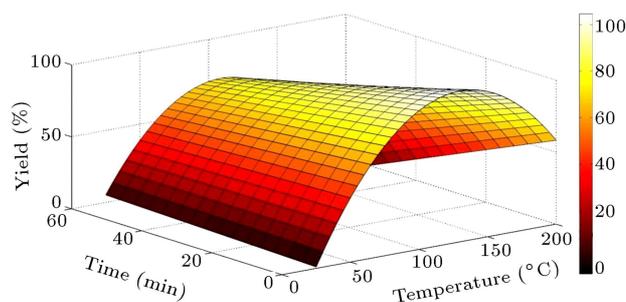
Table 1. The optimization of reaction condition.


Entry	Catalyst	Solvent	Condition	Time (min)	Yield (%) ^a
1	SBA-IL	EtOH	Reflux	180	N.R
2	SBA-IL	-	r. t.	180	N.R
3	SBA-IL	-	100°C	60	50
4	SBA-IL	-	120°C	60	57
5	SBA-IL	-	130°C	60	65
6	SBA-IL	-	150°C	5	95
7	SBA-IL	-	160°C	5	90
8	-	-	160°C	60	25
9	SBA-IL	-	MW (800 W)	8	94

^aIsolated yields

ature on the model reaction of isatin **1**, malononitrile **2**, and 2-hydroxy-1,4-naphthoquinone **3** in the presence of SBA-IL as the catalyst (Table 1). Using ethanol as the solvent was found to be ineffective on this reaction, resulting in a trace of the desired product after the reaction time was extended to 180 min (Table 1, entry 1). We then focused on reaction temperature for further investigation (Table 1, entries 2-7). The best result was obtained at the temperature of 150°C under solvent-free condition (Table 1, entry 6). Increasing the reaction temperature to 160°C did not increase the yield, significantly (Table 1, entry 7). We also studied catalyst-free system at 160°C to screen the presence of catalyst. As shown in Table 1, entry 8, it was found that without any catalyst, only 25% product yield would be achieved after 60 min. At the final evaluation step, we repeated the model reaction under microwave irradiation, which resulted in the isolation of the desired product in 94% yield within 8 min (Table 1, entry 9). The amount of catalyst required for this reaction was also estimated. The model reaction was tested in the presence of 0.01, 0.02, 0.03, and 0.04 g of catalyst and it was found that using 0.02 g of SBA-IL as the catalyst under the optimized conditions was sufficient for the progress of the reaction. Increasing the amount of nanocatalyst to more than 0.02 g had no significant effect on the yield.

Figure 2 shows the synthesis of pyranonaphthoquinone-fused spirooxindole **4a** as a function of the temperature and time. It can be seen that the yield of **4a** increases with increase in reaction temperature until 150°C, which is the optimum point. After this point, increasing the reaction temperature did not show a positive effect on the product yield, which could be due to decomposition of the product at higher

**Figure 2.** Synthesis of pyranonaphthoquinone-fused spirooxindole **4a** as a function of the temperature and time.

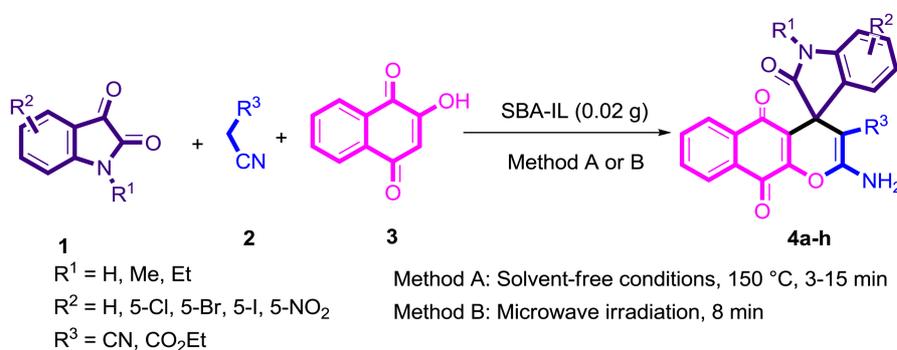
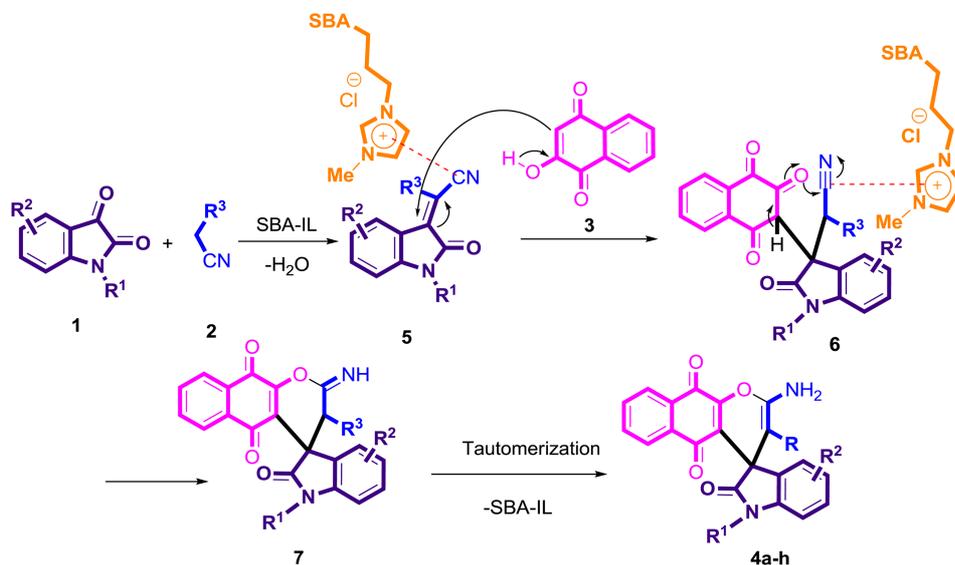
temperature. As clearly visible in this figure, the yield of compound **4a** was powerfully influenced by reaction temperature and time of the multicomponent process. In fact, due to the presence of SBA IL as a nano-reactor in this reaction, the reaction time was very short.

The optimized reaction conditions were then employed for library construction with seven isatin derivatives and two activated methylene reagents (Scheme 2). The corresponding pyranonaphthoquinone-fused spirooxindoles were synthesized successfully in high yields under both solvent-free conditions at 150°C and microwave irradiation. The results are summarized in Table 2. It was observed that isatins having either electron-donating (alkyl) or electron-withdrawing groups (halides) were well tolerated in the corresponding reaction.

A schematic illustration of the proposed mechanism for the catalytic efficiency of SBA-IL on the synthesis of pyranonaphthoquinone-fused spirooxindoles is shown in Scheme 3. It is reasonable to assume that first, the Knoevenagel condensation of isatin **1** and activated methylene reagents **2** in the presence of

Table 2. One-pot three-component synthesis of pyranonaphthoquinone-fused spirooxindoles in the presence of SBA-IL.

No	R ¹	1R ²	R ³	Method A ^a		Method B ^b	m.p. (°C)	m.p. (°C)
				Time (min)	Yield (%)	Yield (%)		
4a	H	H	CN	5	95	94	293-295 (dec)	295 (dec) [19]
4b	H	5-Cl	CN	5	93	90	258-260 (dec)	224-226 [21]
4c	H	5-Br	CN	5	87	85	275-278 (dec)	275 (dec) [19]
4d	H	5-I	CN	15	94	90	262-263 (dec)	New
4e	H	5-NO ₂	CN	10	95	-	288-291 (dec)	290 (dec) [19]
4f	Me	H	CN	3	97	95	263-266 (dec)	265 (dec) [19]
4g	Et	H	CN	3	96	92	208-210 (dec)	211 (dec) [19]
4h	H	H	CO ₂ Et	15	93	-	266-267	268-270 [38]

^aMethod A: Reaction condition: solvent-free at 150°C^bMethod B: Reaction condition: microwave irradiation for 8 minutes**Scheme 2.** Synthesis of pyranonaphthoquinone-fused spirooxindoles in the presence of SBA-IL.**Scheme 3.** Proposed reaction mechanism for the formation of pyranonaphthoquinone-fused spirooxindoles.

SBA-IL provides intermediate **5**. Then, intermediate **5** undergoes Michael-type addition of 2-hydroxy-1,4-naphthoquinone **3** to give intermediate **6**. The following cyclization of hydroxyl group to the cyano moiety and tautomerization leads to the final products **4a-h** [19].

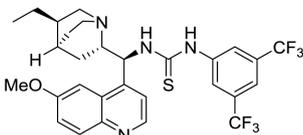
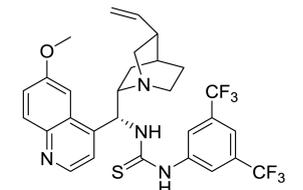
Table 3 illustrates a comparison of the catalytic efficiencies of SBA-IL and other catalysts used in the

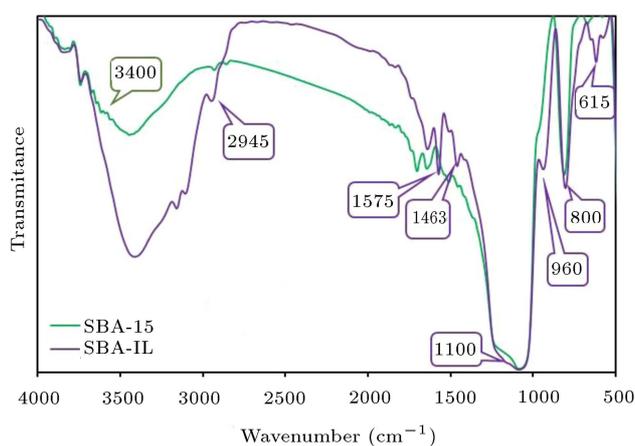
synthesis of pyranonaphthoquinone-fused spirooxindole **4a**. The results clearly indicate that the catalytic activity of SBA-IL is comparable and even superior to other existing methods (Table 3).

3.2. Catalyst identification

The structure of SBA-IL was characterized by SEM, FT-IR, nitrogen adsorption-desorption, and TGA anal-

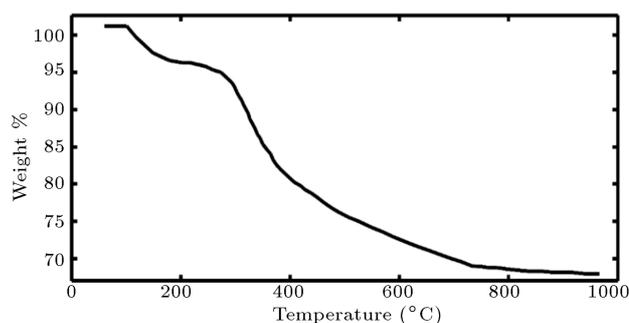
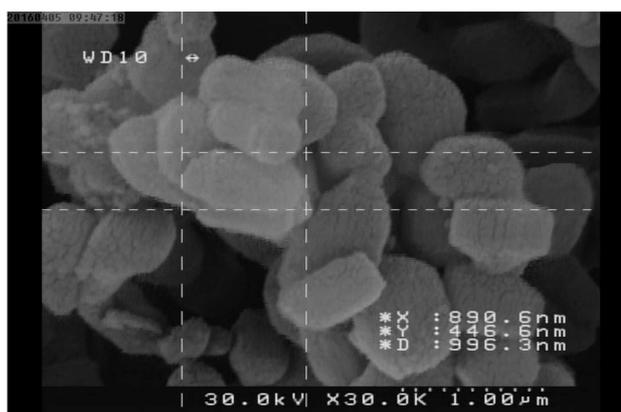
Table 3. Catalytic comparison of SBA-IL with some reports in the literature for the synthesis of pyranonaphthoquinone-fused spirooxindole **4a**.

Entry	Catalyst	Solvent	Condition	Time (h)	Yield (%)	Year (Ref.)
1	<i>p</i> -TSA	H ₂ O	Reflux	7	90	2009 [19]
2	TBAB ^a	H ₂ O	Reflux	55 min	85	2011 [20]
3		Et ₂ O	r.t.	48	98	2014 [21]
4		Toluene	r.t.	120	81	2015 [22]
5	SBA-IL	-	150°C	5 min	95	This work

^aTetrabutyl ammonium bromide.**Figure 3.** FT-IR spectra of SBA-15 and SBA-IL.

yses. Figure 3 shows the FT-IR spectra of SBA-15 and SBA-IL. As illustrated, both materials exhibit characteristic bands of mesoporous silica type materials, i.e., the bands at 800, 960, 1100, and a wide peak at 3400 cm⁻¹. The FTIR spectrum of SBA-IL showed new bands at 2945 cm⁻¹ attributed to the vibrations of the -CH₂- groups of the propyl chains. Moreover, new bands at around 615, 1463, and 1575 cm⁻¹ are related to the mono 4-substituted imidazole, C-H asymmetric stretch, and C=C, C=N aromatic stretching vibrations, respectively. Thus, all observations confirm the successful grafting of imidazolium groups onto the pore walls of SBA-15.

The thermogram of SBA-IL shows several degradation steps corresponding to different mass losses (Figure 4). The initial degradation stage up to around 150°C is due to the removal of adsorbed H₂O molecules from the catalyst. The subsequent major weight loss corresponds to the thermal decomposition of grafted

**Figure 4.** TGA curve of SBA-IL.**Figure 5.** SEM image of SBA-IL.

propyl imidazolium groups, which is estimated to be about 2.0 mmol g⁻¹.

SEM images of SBA-IL are shown in Figure 5. As shown, SBA-IL exhibited uniformly sized pores about 1-2 μm, very similar to those of pure SBA-15, revealing the maintenance of morphology after surface functionalization.

The physical properties of the surface and poros-

Table 4. Textural properties of SBA-15 and SBA-IL.

Sample	S_{BET}^a ($\text{m}^2 \cdot \text{g}^{-1}$)	V^a ($\text{cm}^3 \cdot \text{g}^{-1}$)	D_{BJH}^a (nm)
SBA-15	587	0.780	6.2
SBA-IL	71	0.128	5.5

^a S_{BET} : specific surface area; V : total pore volume; D_{BJH} : average pore diameter.

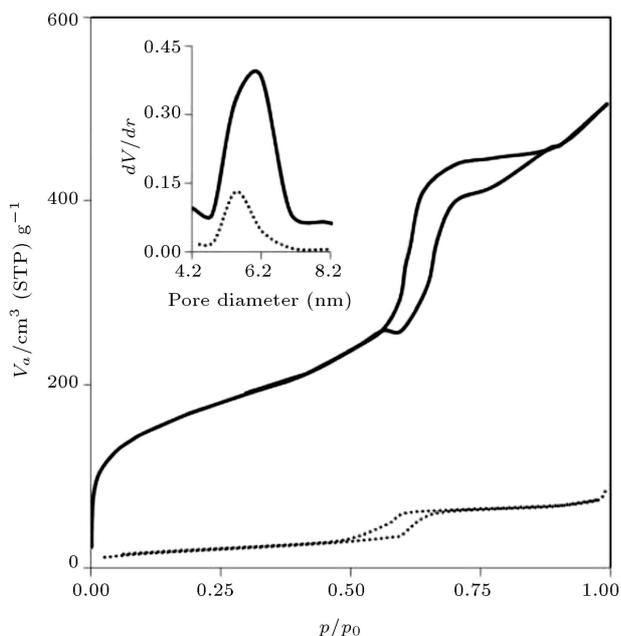


Figure 6. N_2 adsorption-desorption isotherms of (a) SBA-15 and (b) SBA-IL. Inset: BJH pore size distribution curves.

ity variations of SBA-15 were further studied by recording the N_2 adsorption-desorption isotherm of SBA-15 before and after the functionalization step (Figure 6) [32]. As shown, both isotherms exhibited a shape which was in agreement with the type IV nitrogen adsorption-desorption isotherms with H1 hysteresis loops corresponding to mesoporous materials [39]. This observation clearly confirms the preservation of the original structure of SBA-15 after functionalization. Table 4 provides the textural parameters of the samples. A decreasing trend in the three parameters confirmed successful grafting of organic moieties on the surface of SBA-15.

3.3. Catalyst reusability

Lastly, the recyclability of SBA-IL for the preparation of model product **4a** was examined under the optimized conditions (solvent-free conditions at 150°C). For this purpose, the catalyst was separated through a simple filtration after the first reaction run, washed with EtOH, and dried under vacuum. Then, the recovered catalyst was reused for the next run of the reaction. The recycling of the catalyst was carried out up to four reaction runs (Figure 7). The isolated yields for

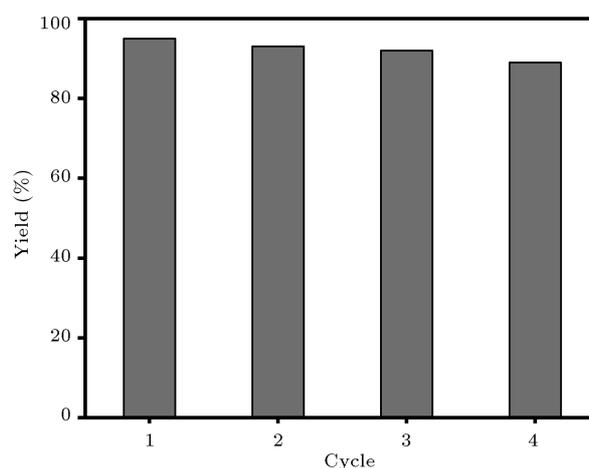


Figure 7. Recyclability of SBA-IL catalyst.

the four runs were found to be 95, 93, 92, and 89%, respectively.

4. Conclusions

An efficient synthesis of desired pyranonaphthoquinone-fused spirooxindoles was achieved via a one-pot three-component reaction of corresponding isatins, activated methylene reagents, and 2-hydroxynaphthalene-1,4-dione under both conventional heating and microwave irradiation in the presence of SBA-IL as a heterogeneous nanocatalyst. Excellent chemical yields, shorter reaction profiles, mild reaction condition, recyclability of the catalyst, and easy workup procedures make the proposed method a sustainable alternative.

Acknowledgments

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