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Preparation and characterization of ionic liquid functionalized SBA-15 and its application in the synthesis of 2,3-dihydroquinazolinones

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ABSTRACT

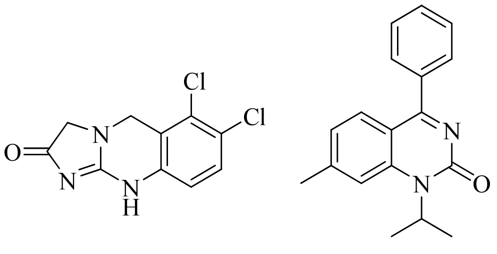
N-Methyl-*N*′-propyltrimethoxysillylimidazolium chloride was prepared as ionic liquid (IL) containing silylating agent and then used for modification of the internal surface of SBA-15 to gain a heterogeneous ionic liquid catalyst. Subsequently, the obtained SBA-IL was characterized using various techniques, including SEM and TEM images, FT-IR, X-ray diffraction, TGA/DTA and BET analyses. It was found that the uniform SBA-15 particles, with a dimension of 400-800 nm, showed the decreasing in the pore volume, surface area, and pore diameter after modification process which is as a results of incorporating imidazole groups onto the pores of SBA-15. Afterward, catalytic activity of SBA-IL was investigated in the synthesis of 2,3-dihydroquinazolinones under solvent free condition.

Keywords: *Quinazoline, SBA-15 functionalized ionic liquid, Nano-catalyst, Isatoic anhydride, One-pot reaction.*

1. Introduction

Santa Barbara Amorphous (SBA) mesoporous silica was firstly synthesized by Zhao and coworkers in 1998 [1]. So far, different members of this family have been produced, which among them SBA-15 is the most applicable mesoporous material in various fields of scientific research [2]. Correspondingly, the surface of SBA-15 is modifiable by the use of alkoxysilanes, and thus, it has been used as catalyst [3-8], adsorbent [9], chemosensor [10-12], and so on.

Quinazoline compounds are important molecules in heterocyclic chemistry because of their biological properties such as sedative-hypnotic [13] anti-inflammatory, analgesic [14], antitumor [15] and anticancer [16] activities. Anagrelide **1** and proquazone **2** (Fig. 1) are quinazoline based drugs which are used for treatment of lukemia and pain, respectively [17,18]. 2,3-Dihydroquinazoline-4(1*H*)-ones are significance class of quinazoline compounds. Due to the importance of such compounds especially in drug discovery [19,20], their synthesis has been developed through the modification of Niementowski reaction [21]. Therefore, using the reaction of isatoic anhydride with a variety of amines and aldehydes or ketones, new derivatives of 2,3-dihydroquinazoline-4(1*H*)-one are obtained [22]. In this paper, SBA-15 was functionalized with *N*-methyl-*N*′-propyltrimethoxy sillylimidazolium chloride as ionic liquid (IL) agent and then applied as catalyst for the multicomponent synthesis of 3-(2′-benzothiazolyl)-2,3-dihydro quinazolin-4(1*H*)-ones.



1
anagrelide

2
proquazone

Fig. 1. Representative examples of quinazoline based drugs.

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2. Experimental

All chemicals employed in this work were purchased from Merck Company and were used without further purification. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$, MW = 5800) (P123) was obtained from Aldrich. Tetraethylorthosilicate (TEOS), *N*-methyl-imidazole, 3-(chloropropyl)trimethoxysilane, dichloromethane and hydrocholoric acid were obtained from Merck Company.

2.1. Instruments and Spectroscopic Measurements

Surface area was measured using the Brunnauer-Teller (BET) method, pore size distributions were calculated from the nitrogen isotherms by Barret-Joyner-Halenda (BJH) method. FT-IR spectra were recorded on the KBr and/or NaCl disks by a FT-IR Bruker Tensor 27 instrument. Melting points were measured using the capillary tube method by an electro thermal 9200 apparatus. The ^{1}HNMR and ^{13}CNMR was run on a Bruker DPX, 300 MHz (for ^{1}HNMR), 75 and 62.5 MHz (for ^{13}CNMR) using TMS as an internal standard (DMSO-d_6 solution). Mass analysis was performed on a Network mass-selective detector (Agilent) 6890/5973. The surface morphologies of samples were observed by a field emission scanning electron microscope (FESEM, Hitachi S-4160 Japan). Thermogravimetric analysis (TGA) was carried out by a BÄHR Thermoanalyse, STA503 model from ambient temperature to 1000 ºC with a ramp rate of 10 ºC min^{-1} in air. Elemental analyses were performed using an Elementar Vario EL III instrument.

2.2. Preparation of ionic liquid supported mesoporous silica (SBA-IL)

2.2.1. Synthesis of the mesoporous silica SBA-15

SBA-15 material was synthesized according to the procedure reported in the literature [23-25]. FT-IR (NaCl): $\bar{\nu}$ = 3434 (O-H stretch), 1086 (Si-O-Si asymmetric stretch), 814 (Si-O-Si symmetric stretch) cm^{-1}.

2.2.2. Synthesis of N-methyl-N′-propyltrimethoxysilyl imidazolium chloride

The *N*-methyl-*N′*-propyltrimethoxysilylimidazolium chloride **3** was prepared by a mixture of *N*-methylimidazole **1** (6.57 g, 80 mmol) and 3-(chloropropyl)trimethoxysilane **2** (15.89 g, 80 mmol) that was stirred in a dry 100 mL flask under inert atmosphere (Ar) at 95 ºC for 24 h. After cooling to room temperature, the resulting liquid product was extracted with ether which then evaporated and the final compound was obtained as a yellow liquid (Scheme 1). FT-IR (NaCl): $\bar{\nu}$ = 2950 and 2853 (C-H asymmetric and symmetric stretches, respectively), 1568 (C=C, C=N), 1457 (C-H bending stretch), 1373 (CH_3 bending stretch), 625 (mono 4-subistituted imidazole) cm^{-1}.

2.2.3. Preparation of imidazolium functionalized SBA-15 (SBA-IL)

SBA-IL was synthesized through the procedure reported in literature [26]. Briefly, the reaction was carried out under inert atmosphere (Ar) in a flask that equipped with a reflux condenser and a magnetic stirrer. Calcined SBA-15 (2.0 g) was activated under reduced pressure at 100 °C for 2 h to remove the adsorbed water. The activated SBA-15 was added to the dried toluene (100 mL) and stirred for 30 min, and *N*-methyl-*N′*-propyl trimethoxysilyl imidazolium chloride **3** (5.61 g) was then added to the resulting mixture. This solution was stirred for 48 h under inert atmosphere (Ar). Afterwards, toluene was removed and the crude SBA-IL was washed with boiling dichloromethane using a Soxhlet apparatus for 48 h, followed by drying under vacuum to remove dichloromethane.

2.2. General procedure for the preparation of 3-(2′-benzothiazolyl)-2,3-dihydroquinazolin-4(1H)-ones derivatives (7a-g)

SBA-IL (0.02 g) was activated under reduced pressure at 100 ºC and after cooling to room temperature, isatoic anhydride **4** (1 mmol), 2-aminobenzothiazole **5** (1 mmol), and benzaldehyde derivative **6a-j** (1.1 mmol) were added to it. The mixture was heated at 130 ºC under solvent free condition for appropriate time as shown in Table 2. When the reaction was completed (monitored by TLC technique), the crude solid product was dissolved in hot EtOH and then filtered for removal of the unsolvable catalyst. The filtrate was cooled to afford the pure product.

Selected spectral data

*3-(2′-benzothiazolyl)-2,3-dihydro-2-(2,3-dicholorophenyl)-quinazolin-4-(1H)-one (**7e**):*

FT-IR (KBr): $\bar{\nu}$ = 3378 (NH), 3066, 1642 (C=O), 1618, 1512, 1387, 1239, 1048, 1003, 737 cm^{-1}. ^{1}HNMR (300 MHz, DMSO-d_6): δ= 8.16 (d, *J*= 4.3 Hz, 1H, NH), 8.00 (d, *J*= 7.7 Hz, 1H, ArH), 7.91 (d, *J*= 7.7 Hz, 1H, ArH), 7.73 (d, *J*=4.3 Hz, 1H, CH (sp^3)), 7.69 (d, *J*= 7.9 Hz, 1H, ArH), 7.53 (d, *J*= 7.5 Hz, 1H, ArH), 7.37 (m, 2H, ArH), 7.30 (t, *J*= 7.5 Hz, 1H, ArH), 7.18 (t, *J*= 7.9 Hz, 1H, ArH), 7.03 (d, *J*= 7.3 Hz, 1H, ArH), 6.87 (d, *J*= 8.3 Hz, 1H, ArH), 6.82 (d, *J*= 7.5 Hz, 1H, ArH) ppm. ^{13}CNMR (75MHz, DMSO-d_6): δ= 135.74, 132.97, 132.55, 130.72, 129.70, 128.43, 128.35, 126.29, 124.25, 124.05, 121.72, 121.14, 118.77, 116.02, 112.77 ppm. MS (EI): m/z= 425 (16%), 390 (14%), 291 (100%), 276 (94%), 254 (20%), 211 (25%), 186 (36%), 149 (25%), 130 (24%), 105 (30%), 77 (29%). Anal. Calc. for $C_{21}H_{13}N_{3}Cl_{2}SO$, Found: C 59.21, H 3.10, N 9.89, Requires: C 59.16, H 3.07, N 9.86.

*3-(2'-benzothiazolyl)-2,3-dihydro-2-(2,3-dimethoxyphenyl)-quinazolin-4-(1H)-one (**7f**).*

FT-IR (KBr): $\bar{\nu}$ = 3398 (NH), 3057, 2995, 2825, 1644 (C=O), 1616, 1512, 1386, 1271, 1239, 1005, 753 cm^{-1}. ^{1}HNMR (300 MHz, DMSO-d_6): δ= 8.00 (d, *J*= 7.8 Hz, 1H, ArH), 7.86 (d, *J*= 7.8 Hz, 1H, ArH), 7.80 (d, *J*= 3.8 Hz, 1H, NH), 7.71 (d, *J*= 9.3 Hz, 1H, ArH), 7.67 (d, *J*= 4.1 Hz, 1H, CH(SP^3)), 7.42 (m, 3H, ArH), 6.95 (d, *J*= 8.1 Hz, 1H, ArH), 6.87 (d, *J*= 7.9 Hz, 1H. ArH), 6.83 (t, *J*= 7.9 Hz, 1H, ArH), 6.78 (t, *J*= 7.7 Hz, 1H, ArH), 6.52 (d, *J*= 7.6 Hz, 1H, ArH) ppm. ^{13}CNMR (62.5 MHz, DMSO-d_6): δ= 56.29, 60.88, 65.45, 113.20, 113.89, 116.11, 117.21, 118.56, 121.39, 122.16, 124.25, 124.21, 126.70, 128.67, 133.74, 135.94, 146.38, 146.70, 148.10, 15.20, 157.58, 162.48 ppm. MS (EI): m/z= 417 (22%), 386 (15%), 364 (15%), 283 (100%), 268 (81%), 196 (44%), 182 (41%), 149 (87%), 132 (57%), 105 (58%), 92 (40%), 77 (38%). Anal. Calc. for $C_{23}H_{19}N_{3}SO_{3}$, Found: C 66.23, H 4.65, N 10.11, Requires: C 66.17, H 4.59, N 10.07.

*3-(2'-benzothiazolyl)-2,3-dihydro-2-(2,4-dicholorophenyl)-quinazolin-4-(1H)-one (**7g**).*

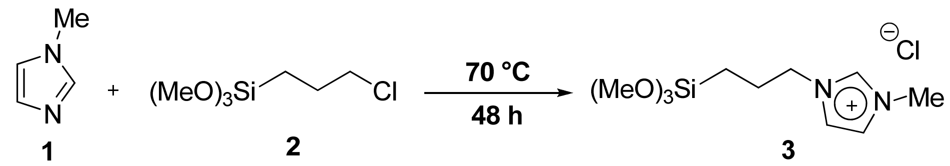
FT-IR (KBr): $\bar{\nu}$ = 3414 (NH), 3064, 1661 (C=O), 1614, 1501, 1398, 1240, 1105, 854, 820, 746 cm^{-1}. ^{1}HNMR (300 MHz, DMSO-d_6) δ= 8.12 (d, *J*= 4.4 Hz, 1H, NH), 8.00 (d, *J*= 7.8 Hz, 1H, ArH), 7.90 (d, *J*= 7.3 Hz, 1H, ArH), 7.70 (d, *J*= 7.5 Hz, 1H, CH), 7.68 (d, *J*= 2.13 Hz, 1H, ArH), 7.65 (d, *J*= 4.3 Hz, 1H, ArH), 7.40 (m, 2H, ArH), 7.31 (t, *J*= 7.5 Hz, 1H, ArH), 7.26 (d.d, *J*= 8.4, 2.1 Hz, 1H, ArH), 7.05 (d, *J*= 8.4 Hz,1H, ArH), 6.87 (d, *J*= 7.9 Hz, 1H, ArH), 6.81 (t, *J*= 7.2 Hz, 1H, ArH) ppm. ^{13}C NMR (62.5 MHz, DMSO-d_6): δ= 66.07, 113.26, 116.47, 119.22, 121.55, 122.16, 124.70, 126.73, 127.28, 128.79, 130.37, 133.00, 133.15, 134.47, 136.18, 136.28, 145.82, 147.85, 157.19, 162.02 ppm. M (EI): m/z= 425 (16%), 390 (8%), 291 (100%), 276 (91%), 254 (20%), 211 (20%), 186 (33%), 149 (27%), 105 (24%), 77 (22%). Anal. Calc. for $C_{21}H_{13}N_{3}Cl_{2}SO$, Found: C 59.25, H 3.15, N 9.93, Requires: C 59.16, H 3.07, N 9.86.

3. Results and Discussion

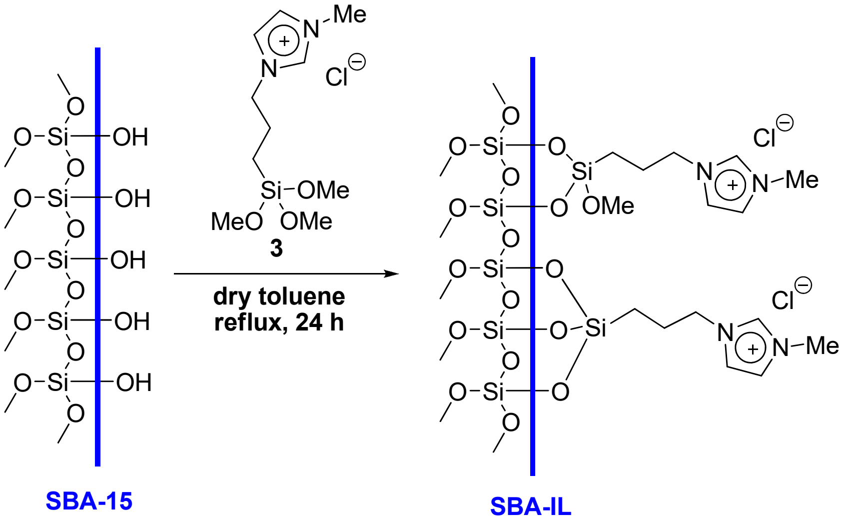
3.1. Preparation and characterization of SBA-IL

Up to now, the surface of silica has been modified with imidazolium groups and used in some organic reactions [27-30], nevertheless, since the outer surface of silica is modified, the leaching phenomenon is occurred as a result of mechanical impact during the reaction. To overcome this drawback, herein, mesoporous SBA-15 was used and its internal surface was modified with imidazolium group to minimize the leaching effect and thus its recyclability is guaranteed. Therefore, SBA-15 was initially synthesized through the procedure reported in the literature [31-33]. Compound **3** was also prepared through the reaction of *N*-methylimidazole **1** and 3-(chloropropyl)trimethoxy silane **2** under inert atmosphere (Ar) at 70 ºC (Scheme 1). Then, the *N*-methyl-*N'*-propyltrimethoxy silylimidazolium chloride **3** was added to the calcined and activated SBA-15 to produce the functionalized SBA-IL (Scheme 2). The surface of the catalyst was analyzed by different methods such as BET, BJH methods, TGA-DTA, FT-IR, XRD and, SEM and TEM images which demonstrated that the organic groups were immobilized into the pores.

Properties of the SBA-15 and SBA-IL were evaluated by the nitrogen adsorption-desorption isotherms (Fig. 2). Both of them exhibit a typical irreversible type IV nitrogen adsorption isotherm with an H1 hysteresis loop as defined by IUPAC [34]. Additionally, a shift of the hysteresis position is seen toward low relative pressures and also the adsorption volume of SBA-IL shows a slightly decreasing trend in overall nitrogen due to the loading of imidazole groups onto the internal pores of SBA-15. The pore size distribution can be obtained by BJH method according to the desorption branch of the N_2 adsorption isotherm. The uniformity of the pores in SBA-IL is comparable to the SBA-15, indicating that the original inorganic wall structure of the SBA-15, is retained. Moreover, the pore diameter of SBA-IL decreases by about 0.7 nm.



Scheme 1. Synthesis of *N*-methyl-*N'*-propyl trimethoxysilylimidazolium chloride.



Scheme 2. Preparation of functionalized SBA-15 (SBA-IL).

The textural parameters including pore diameters (BJH method), specific surface areas (S_{BET}), and total pore volumes are given in Table 1, which show the decreasing in pore volume, surface area, and pore diameter due to the presence of imidazole groups onto the pores SBA-IL.

The TGA-DTA analysis of SBA-IL (Fig. 3) proved that the organic functional groups (propyl imidazolium) were grafted onto the pores of SBA-15. The first mass loss happened between 100 and 300 °C, corresponding to an endothermic peak at 120 °C in the DTA plot. This mass loss is due to the removal of physically absorbed water and solvent used in the synthetic procedure which were not removed during drying process.

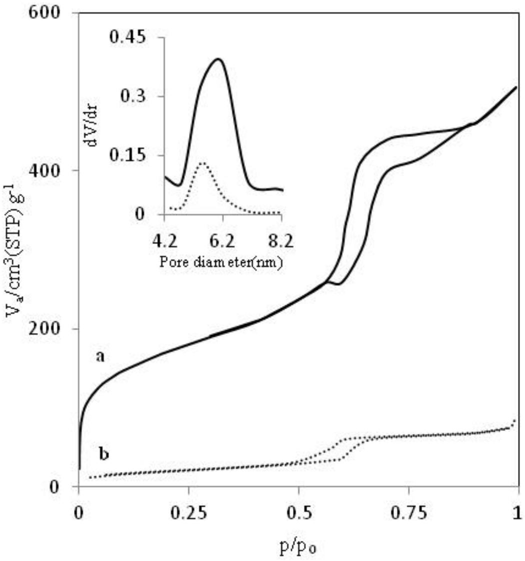


Fig. 2. N_2 adsorption-desorption isotherms of (a) SBA-15, (b) SBA-IL; (inset) BJH pore size distribution curves.

Additional weight loss that happening from the end of first mass loss with an exothermic peak till around 450 °C is reflected by a sharp endothermic peak at 334 °C and might be attributed to the decomposition of the organic groups. The third mass drop (onset at 630 °C) till around 710 °C is due to the removal of HCl gas and condensation of silanol groups. Subsequently, the weight loss at the temperature range between 280-700 °C indicates that the amount of propyl imidazolium groups is 1.07 mmol/g.

SEM image of SBA-IL (Fig. 4) shows rice-like uniform particles with dimensions about 400-800 nm. The same morphology was previously observed for SBA-15. Thus it was proved that the morphology of SBA-IL was preserved without any changes during the modification procedure.

Fig. 5 shows the low angle XRD patterns of SBA-15 and SBA-IL materials. As can be seen, this sample has a single intensive reflection at 2θ angle around 0.85° similar to the typical SBA-15 materials that is generally attributed to the long-range periodic and two additional peaks corresponding to the higher ordering (110) and (200) reflections which is associated with a two-dimensional hexagonal (p6mm) structure.

Table 1. The pore diameters (D_{BJH}), BET surface area (S_{BET}) and the total pore volumes (V_{total}) from nitrogen adsorption-desorption for the SBA-15 and SBA-IL.

Molecular sieves	D_{BJH}(nm)	S_{BET}(m^2/g)	V_{total}(cm^3/g)
SBA-15	6.2	587	0.780
SBA-IL	5.5	71	0.128

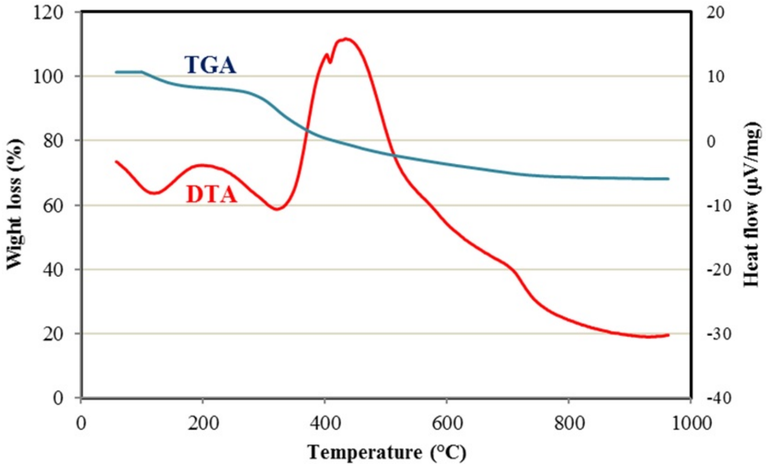


Fig. 3. TGA and DTA analysis of SBA-IL.

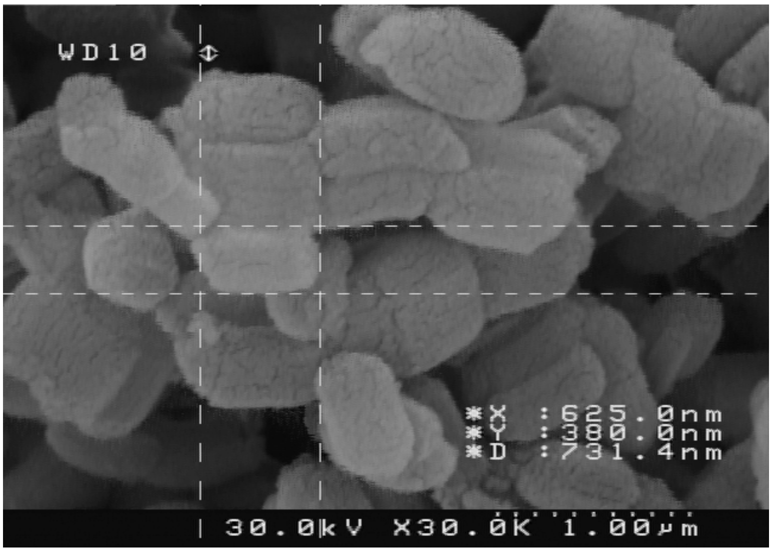


Fig. 4. SEM image of SBA-IL.

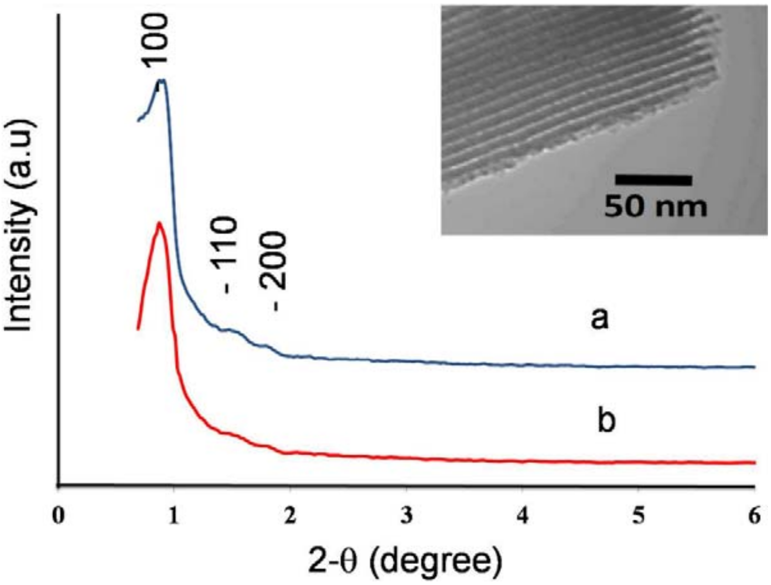


Fig. 5. XRD patterns of a) SBA-15 and b) SBA-IL. The inset is the TEM image of SBA-Ionic liquid.

However, the decrease in the intensity of the (100), (110) and (200) diffractions in SBA-ionic liquid may be due to the reduction in scattered X-ray radiation resulting from covering the surface with the attachments of the organic moieties. The Fig. 5 inset shows the TEM image of SBA-15 which displays two dimensional channels throughout the particle with a pore diameter of approximately 5 nm.

By comparing the FT-IR spectra of both SBA-15 and SBA-IL (Fig. 6), surface modification of SBA-15 with IL is completely obvious. The absorption bands at 1100, 960 and 800 cm^{-1} attribute to the Si–O–Si asymmetric stretching, S–OH symmetric stretching and Si–O symmetric stretching vibrations, respectively. A broad absorption band at 3403 cm^{-1} is as a results of the quaternary amine salt vibration. The absorption band at 3107 cm^{-1} corresponds to the vibration of -HC=CH- aromatic ring in imidazolium moiety. The band at 2948 cm^{-1} is for asymmetric vibration of CH_2 and CH_3 of organic groups grafted onto the SBA-IL. Additionally, the band at 1569 cm^{-1} is for out of plane stretching vibration of N-Me in imidazolium group.

3.2. The use of SBA-IL as catalyst in the synthesis of dihydroquinazolinones

In this paper, solvent-free one-pot reaction of isatoic anhydride **4**, 2-aminobenzothiazole **5** and benzaldehyde derivatives **6a-j** was studied in the presence of SBA-IL (Scheme 3). As shown by the results in Table 2, among the tested solvents and the solvent-free system, the best result was achieved under solvent-free condition at 130 °C. To investigate the effect of imidazole groups onto the SBA-IL pores, the reaction was run in the presence of pure SBA-15. The surface of SBA-15 has silanol groups which have poor acidic properties, consequently, it can act as a catalyst singly. Although the reaction time in the presence of SBA-15 is 75 min, SBA-IL reduced the time to 15 min. Also, the product yield using SBA-15 is lower than that of obtained by SBA-IL. Hence, the surface modification of SBA-15 to gain SBA-IL was a good plan to increase its catalytic activity. In addition, the reaction didn't proceed in the absence of the catalyst within 75 min. Therefore, in order to study generality of this reaction, it was performed with different benzaldehyde derivatives; the results are summarized in Table 3. When the reaction was completed, the product was dissolved in hot EtOH, and then, the catalyst was separated by a simple filtration and reused. The new products were characterized by FT-IR, Mass, ^{1}HNMR and ^{13}CNMR spectroscopy data. Melting points were compared with values which reported in the literature (Table 3).

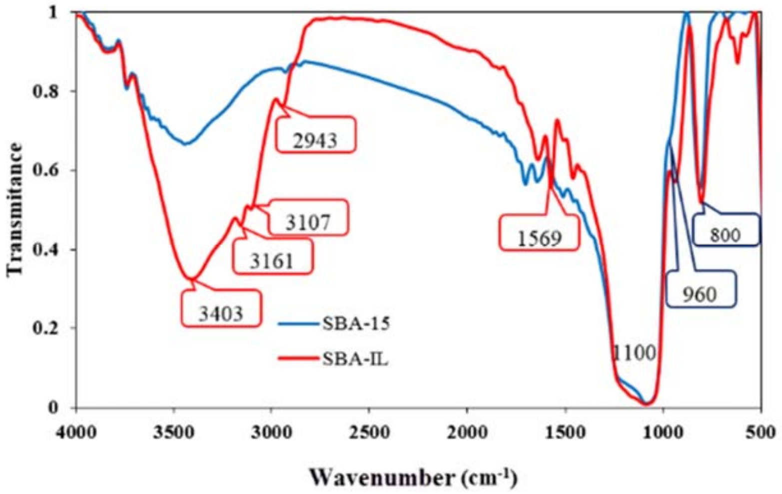
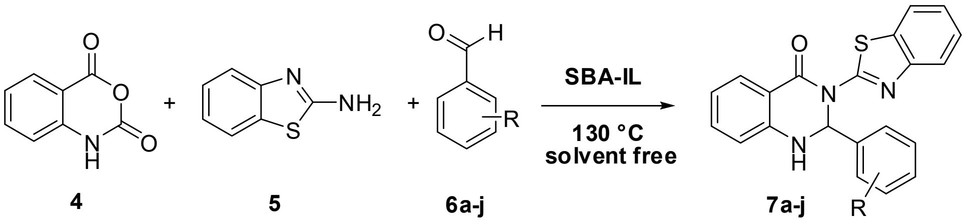


Fig. 6. FT-IR spectra of SBA-15 and SBA-IL.



Scheme 3. General synthesis of 3-(2′-benzothiazolyl)-2,3-dihydroquinazolin-4(1*H*)-ones.

Table 2. Reaction optimization for the synthesis of product **7a**.

Entry	Catalyst	Solvent	Condition	Time (h)	Yield (%)
1	SBA-IL	EtOH	reflux	10	72
2	″	MeCN	reflux	10	85
3	″	H_2O	reflux	10	81
4	″	-	100 °C	10	87
5	″	-	130 °C	15 min	95
6	SBA-15	-	130 °C	75 min	85
7	-	-	130 °C	75 min	Trace

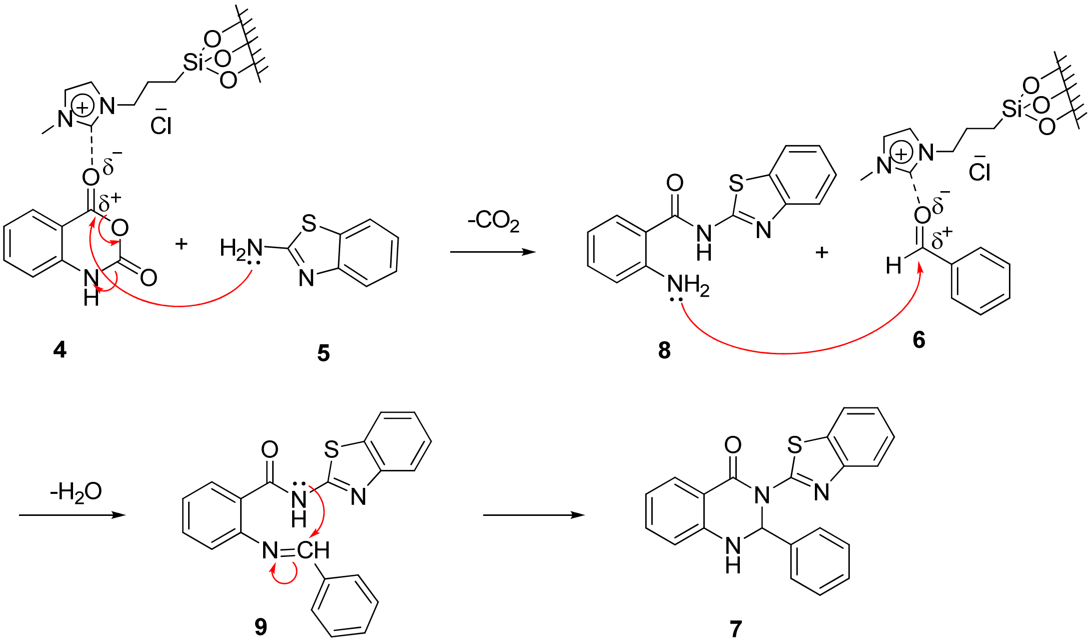
The proposed mechanism for the SBA-IL-catalyzed one-pot reaction is shown in Scheme 4. Concerning the reaction mechanism, it is suggested that, initially, the catalyst activates the carbonyl group of isatioc anhydride, and then, the N-nucleophilic primary amine **5** attacks to the activated carbonyl **4** to produce intermediate **8** after decarboxylation reaction. Subsequently, N-nucleophilic primary amine **8** is added to the activated benzaldehyde carbonyl **6** to generate an imine compound **9**. Thus, the product **7** can be prepared by intermolecular nucleophilic addition of the amide nitrogen to the imine carbon.

The SBA-IL recyclability was examined under the optimized conditions for the synthesis of quinazolinone **7a**. Accordingly, the model reaction was performed in the first run for three times to recover about 0.05 gr SBA-IL. Subsequently, it was well washed with hot EtOH for removal of the adsorbed organic compounds and then reused. The process of recycling was repeated for two times and the yields for the second and third cycles were 87 and 85%. The catalytic activity drop from the first use (95%) to the second (87%) is as a result of leaching the imidazolium groups which were not grafted well on the surface of SBA-15. Moreover, no significant decrease was observed in catalytic activity for the third cycle, which means all the flimsy imidazolium groups were leached during the first stage of the recovery. In fact, this catalyst is completely recoverable.

Literature survey showed that the benzothiazole containing quinazolinone derivatives have been produced under different conditions. In comparison with other methods for the preparation of product **7a**, as mentioned in Table 4, the present method is the best one due to numerous advantages in term of metal-free catalysis, easy separation of the heterogeneous SBA-IL catalyst, and excellent product yield within short reaction time.

Table 3. SBA-IL-catalyzed synthesis of 3-(2′-benzothiazolyl)-2,3-dihydroquinazolin-4(1*H*)-ones.

Entry	No.	R	Time (min)	Yield (%)	m.p. (°C)		Ref.
					Found	Reported	
1	**7a**	2-OMe	15	95	233-234	229-233	[35]
2	**7b**	H	15	81	237-239	233-236	[36]
3	**7c**	4-OMe	15	93	185-187	184-186	[36]
4	**7d**	4-Cl	15	87	206-207	198-200	[35]
5	**7e**	2,3-Cl_2	30	96	249-250	New	
6	**7f**	2,3-$(OMe)_2$	15	88	222-224	New	
7	**7g**	2,4-Cl_2	50	90	237-239	New	
8	**7h**	3-NO_2	15	92	256-257	251-253	[36]
9	**7i**	4-NO_2	15	92	224-226	242-245	[37]
10	**7j**	4-Me	20	86	216-218	198-199	[36]



Scheme 4. The proposed mechanism for the synthesis of quinazolinones in the presence of SBA-IL as catalyst.

Table 4. Comparison of the published methods for the synthesis of product **7a**.

Entry	Catalyst	Solvent	Condition	Yield (%)	Time (min)	Reference
1	SBA-IL	-	130 °C	95	15	This work
2	$Zr(HSO_4)_4$	-	110 °C	89	30	[37]
4	Agar	H_2O:EtOH (3:1)	Reflux	90	40	[38]
5	-	-	130 °C	57	3.15 h	[39]
6	$Al(H_2PO_4)_3$	-	100 °C	80	13	[35]
7	H_3PO_4/Al_2O_3	-	100 °C	93	12	[40]

4. Conclusion

In this study, SBA-15 was produced and then functionalized with imidazolium ionic liquid to gain SBA-IL. Afterwards, SBA-IL was characterized by FT-IR, BET, BJH, TGA-DTA, XRD, and SEM and TEM images and then used as a heterogeneous catalyst in a three-component synthesis of 3-(2′-benzo thiazolyl)-2,3- dihydro quinazolin- 4(1*H*)- ones. The reaction condition was mild which gave the products in excellent yields and easy work-up process. Therefore, this catalyst may be applicable in different organic reactions.

Acknowledgment

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