J IRAN CHEM SOC
DOI 10.1007/s13738-017-1125-x

ORIGINAL PAPER

A simple and convenient synthesis of [1,2,4]triazolo/benzimidazolo quinazolinone and [1,2,4]triazolo[1,5-*a*]pyrimidine derivatives catalyzed by DABCO-based ionic liquids

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Received: 15 October 2016 / Accepted: 13 April 2017

Abstract DABCO-based ionic liquids were utilized for the preparation of [1,2,4]triazolo/benzimidazolo quinazolinone and [1,2,4]triazolo[1,5-*a*]pyrimidine derivatives in the adequate procedures. These methods involve three-component reaction between aldehydes, β-diketones and 3-amino-1,2,4-triazole or 2-aminobenzimidazole in the presence of 1,4-disulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium chloride ($[DABCO](SO_3H)_2(Cl)_2$) and 1,4-disulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium dihydrogen sulfate ($[DABCO](SO_3H)_2(HSO_4)_2$) as reusable and economical catalysts at 100 °C. These methods also show eco-friendly characters by elimination of solvent. Any by-product was not prepared through this method, and products were separated by a simple workup procedure. The other noticeable benefits of these procedures are excellent yields, short reaction times, mild reaction conditions and use of available and inexpensive materials.

Keywords 1,4-Diazabicyclo[2.2.2]octane (DABCO) · DABCO-based ionic liquids · Multi-component reactions (MCRs) · Quinazoline derivatives · 3-Amino-1,2,4-triazole · 2-Aminobenzimidazole

Introduction

In recent years, combinatorial chemistry is widely developed due to its wide applications in generation of drugs. It has appeared as a powerful tool to accelerate generation, identification and optimization of lead compounds in the drug discovery processes [1–3]. Nitrogen-containing heterocycles have been utilized in the pharmaceutical and agrochemical industries widely because of their varied physiological properties [4]. Among these types of compounds, quinazoline derivatives possess important pharmacological activities such as antihypertensive [5], antidiabetics [6], anti-inflammatory [7], antifertility [8], anticonvulsant [9], anticancer [10] and anti-HIV [11]. Besides, benzimidazoles and triazoles are the important structural motif in the skeleton of some biologically active molecules [12–14]. For example, some antifungal medications including fluconazole, itraconazole and albaconazole are adequate examples which possess triazole motif in their structures (Fig. 1).

Although many methods are reported to prepare these compounds, such as refluxing in DMF [15–17] or EtOH [18, 19], solvent-free condition [20], microwave irradiation [21–23], $H_6P_2W_{18}O_{62}{\cdot}18H_2O$ [24], sulfamic acid (NH_2SO_3H) [25], 1-*n*-butyl- 3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$) [26], 1-butyl-3-methylimidazolium bromide ([bmim]Br) [27], molecular iodine (I_2) [28], chitosan-based composite magnetic nanocatalyst [29], *p*-toluenesulfonic acid [30], acetic acid [31], nano-SiO_2 [32] and sulfonic acid functionalized nanoporous silica ($SBA–Pr–SO_3H$) [33], many of them suffer from some disadvantages such as use of expensive and hazardous catalysts [24, 29, 32, 33] or solvent [15–17, 21], harsh conditions [15–20], long reaction time [18, 20, 29] and low yields [15–17, 19, 20]. However, some of these methods are roughly good, but yet it is necessary to improve

Electronic supplementary material The online version of this article (doi:10.1007/s13738-017-1125-x) contains supplementary material, which is available to authorized users.

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Published online: 24 May 2017

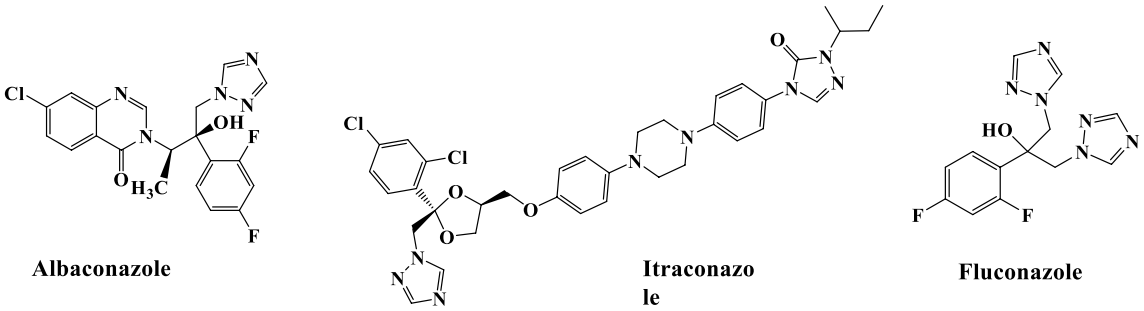


Fig. 1 Some antifungal medications possessing the triazole nucleus

procedures to achieve a simple, efficient, inexpensive and nontoxic procedure with readily available reagents.

One-pot strategies are well known in organic synthesis as efficient processes to access complex molecules without isolating intermediates [34]. These reactions are more interesting for organic chemists because of avoiding sequential separation and purification processes that could save time and resources while increasing chemical yield. As one of the most popular and widely used one-pot strategies, multicomponent reactions (MCRs) are powerful tools in the synthesis of condensed heterocycle molecules. In these reactions, three or more ingredients mix together to provide a product containing the same elements of the all reactants. These reactions can be a very elegant and rapid way to obtain complex structures in a single synthetic throughput from simple building blocks and show high selectivity [35–37].

MCRs gave this opportunity to chemists that could eliminate toxic organic solvents from reaction media. Recently, chemists were interested to research about solid-state reactions as they offer potential reduction in environmental pollution with the elimination of solvents [38, 39]. According to green chemistry principles [40], elimination of solvents can cause to lower toxicity and hazard, decrease waste and save time and resources in the chemical processes.

Nowadays, room-temperature ionic liquids (RTILs) have been used as alternative 'green' solvents instead of hazardous traditional organic solvents, due to their properties such as non-flammability, negligible vapor pressure, high thermal stability, solvating ability and easy recyclability. They have the potential to be highly polar yet non-coordinating [41–45].

Experimental

General

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. Yields refer to the isolated products. Products were characterized by their physical constants in comparison with authentic samples, IR and NMR spectroscopy. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

Instrumentation

Melting points were measured by a Büchi B-545 apparatus in open capillary tubes. FT-IR spectra were recorded on a Perkin-Elmer spectrum BX series. ^{1}H NMR and ^{13}C NMR spectra were determined on Bruker AV-400 spectrometers using TMS as internal standard

Preparation of $[DABCO](HSO_3)_2(Cl)_2$ and $[DABCO](SO_3H)_2(HSO_4)_2$

Chlorosulfonic acid (1.75 g, 15 mmol) was added dropwise to a round-bottom flask (100 mL) containing 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.841 g, 7.5 mmol) in dry CH_2Cl_2 (50 mL), over a period of 5 min in an ice bath. After the completion of addition, the reaction mixture was stirred for 2 h and then stood for 5 min, and then, CH_2Cl_2 was decanted. The residue was washed with dry diethyl ether (3 × 50 mL) and dried under vacuum to give $[DABCO](HSO_3)_2(Cl)_2$ as a white solid in 98% yield [46]. At the second step and in a round-bottom flask (100 mL) containing $[DABCO](HSO_3)_2(Cl)_2$ (0.864 g, 2.5 mmol) equipped with a gas inlet tube for conducting HCl gas over an adsorbing solution (i.e., water), sulfuric acid (99.99%, 0.49 g, 5 mmol) was added dropwise over a period of 5 min in an ice bath. After the addition was completed, the reaction mixture was left for 6 h to give $[DABCO](SO_3H)_2(HSO_4)_2$ as a white solid in 95% yield [47] (Fig. 2). The product was formed quantitatively and in high purity as assessed by melting point, mass, Hammett acidity, FT-IR, ^{1}H NMR, ^{13}C NMR and elementary analysis.

1,4-disulfo-1,4-diazabicyclo[2.2.2]octane-1,4-dium chloride ([DABCO](SO$_3$H)$_2$(Cl)$_2$) White solid; M.p.: 75 (°C); IR (KBr, υ, cm^{-1}) 3500–2800 (O–H, broad), 1177 (S–O), 881 (S–N), 854 (S–O); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.58 (6H, s, CH$_2$), 7.72 (1H, s, SO$_3$H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 43.2; MS: m/z = 345 (M$^+$); H_0 = 1.37; Anal. Calcd for $C_6H_{14}Cl_2N_2O_6S_2$: C, 20.88; H, 4.09; Cl, 20.54; N, 8.12; O, 27.81; S, 18.57.

1,4-disulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium dihydrogen sulfate ([DABCO](SO$_3$H)$_2$(HSO$_4$)$_2$) White solid; M.p.: 70 (°C); FT-IR (KBr, υ, cm^{-1}) 3500–2800 (O–H, broad), 1287 (S–O), 1177 (S–O), 883 (S–N), 854 (S–O); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.59 (6H, s, CH$_2$), 6.97 (1H, s, SO$_3$H), 14.14 (1H, s, HSO$_4$); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 43.2; MS: m/z = 467(M$^+$); H_0 = 0.43; Anal. Calcd for $C_6H_{16}N_2O_{14}S_4$: C, 15.38; H, 3.44; N, 5.98; O, 47.82; S, 27.38.

General procedure for the preparation of benzimidazoquinazolinone derivatives

A mixture of aromatic aldehyde 1 (1.0 mmol), dimedone 2 (1.0 mmol), 2-aminobenzimidazole 3 (1.0 mmol) and [DABCO](HSO$_3$)$_2$(Cl)$_2$ (0.2 mmol, method A) or [DABCO](SO$_3$H)$_2$(HSO$_4$)$_2$ (0.02 mmol, method B) was stirred at 100 °C for the appropriate time. The progress of the reaction was followed by TLC (*n*-hexane/ethyl acetate—8:2). After completion, the obtained solid mixture was washed with cooled water (2 × 2 mL) to separate the catalyst. Then, warm ethanol (3 mL) was added to the reaction media, and the solid product was filtered and dried in air.

General procedure for the preparation of triazoloquinazolinone derivatives

A mixture of aromatic aldehyde 1 (1.0 mmol), 3-amino-1,2,4-triazole 5 (1.0 mmol), β-diketones (dimedone 2, 1,3-cyclohexadione 6 or ethyl acetoacetate 7) (1.0 mmol) and [DABCO](HSO$_3$)$_2$(Cl)$_2$ (0.2 mmol, method A) or [DABCO](SO$_3$H)$_2$(HSO$_4$)$_2$ (0.02 mmol, method B) was stirred at 100 °C for the appropriate time. After completion of the reaction, as indicated by TLC (*n*-hexane/ethyl acetate—8:2), a thick precipitate would be obvious. Then cooled water (2 × 2 mL) was added to the reaction media to separate the catalyst. After washing with water, warm ethanol (3 mL) was added and the solid product was filtered to give the pure product; afterward, it was dried in air. The pure products were characterized by conventional spectroscopic methods. Physical and spectral data for new compounds are represented below.

9-(4-Bromophenyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one 8q White powder; M.p.: 306–308 (°C); IR (KBr, υ, cm^{-1}) 3429 (N–H), 3129 (CH-arom), 2883 (CH-aliph), 1648 (C=O), 1578 (N–H), 621 (C–Br); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.89–2.01 (2H, m, CH$_2$), 2.22–2.34 (2H, m, CH$_2$), 2.61–2.71 (2H, m, CH$_2$), 6.23 (1H, s, CH), 7.18 (2H, d, J = 8.4 Hz, CH-Ph), 7.49 (2H, d, J = 8.4 Hz, CH-Ph), 7.71 (1H, s, CH-triazole), 11.21 (1H, s, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 21.1, 26.8, 36.7, 44.4, 57.7, 106.6, 121.3, 129.7, 131.6, 141.3, 147.1, 150.6, 153.2, 193.8; Anal. Calcd for $C_{15}H_{13}BrN_4O$: C, 52.19; H, 3.80; Br, 23.15; N, 16.23; O, 4.63.

9-(2-Nitrophenyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one 8s White powder; M.p.: 300–304 (°C); IR (KBr, υ, cm^{-1}) 3444 (N–H), 3213 (CH-arom), 2910 (CH-aliph), 1643 (C=O), 1569 (NO$_2$), 1357 (NO$_2$); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.88–1.99 (2H, m, CH$_2$), 2.17–2.27 (2H, m, CH$_2$), 2.64–2.67 (2H, m, CH$_2$), 6.98 (1H, s, CH), 7.30 (1H, d, J = 1.2 Hz, CH-Ph), 7.49 (1H, dt, J_1 = 7.6 Hz, J_2 = 0.8 Hz, CH-Ph), 7.61 (1H, dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, CH-Ph), 7.73 (1H, s, CH-triazole), 7.86 (1H, dd, J_1 = 8 Hz, J_2 = 1.2 Hz, CH-Ph), 11.32 (1H, s, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 21.1, 26.8, 36.4, 53.4, 106.19, 124.4, 129.4, 129.8, 133.8, 135.3, 147.2, 149.0, 150.8, 153.7, 193.9; Anal. Calcd for $C_{15}H_{13}N_5O_3$: C, 57.87; H, 4.21; N, 22.50; O, 15.42.

Results and discussions

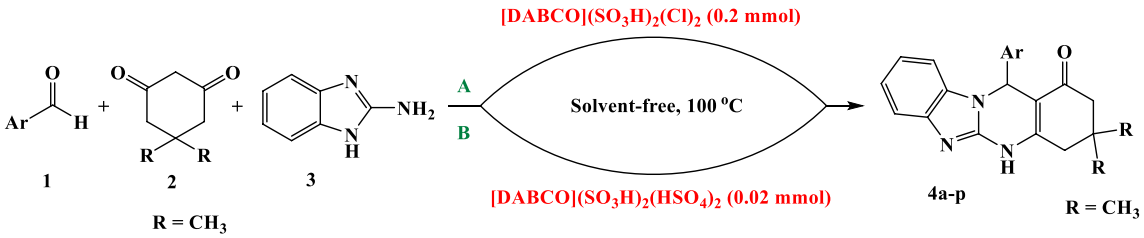
In recent years, preparation and use of *N*-sulfonic acids have become an important part of our ongoing research program [48–55]. In continuation of these studies and of the mentioned difficulties in the synthesis of quinazolinone derivatives, herein we wish to report new and straightforward one-pot procedures to prepare quinazolinone derivatives using [DABCO](SO$_3$H)$_2$(Cl)$_2$ and [DABCO](SO$_3$H)$_2$(HSO$_4$)$_2$ as efficient ionic liquids and compare the ability of these catalysts in the studied reactions.

At first, to find the best reaction conditions and amount of the catalysts, the reaction of 4-chlorobenzaldehyde, dimedone and 2-aminobenzimidazole in the presence of [DABCO](HSO$_3$)$_2$(Cl)$_2$ (method A) and

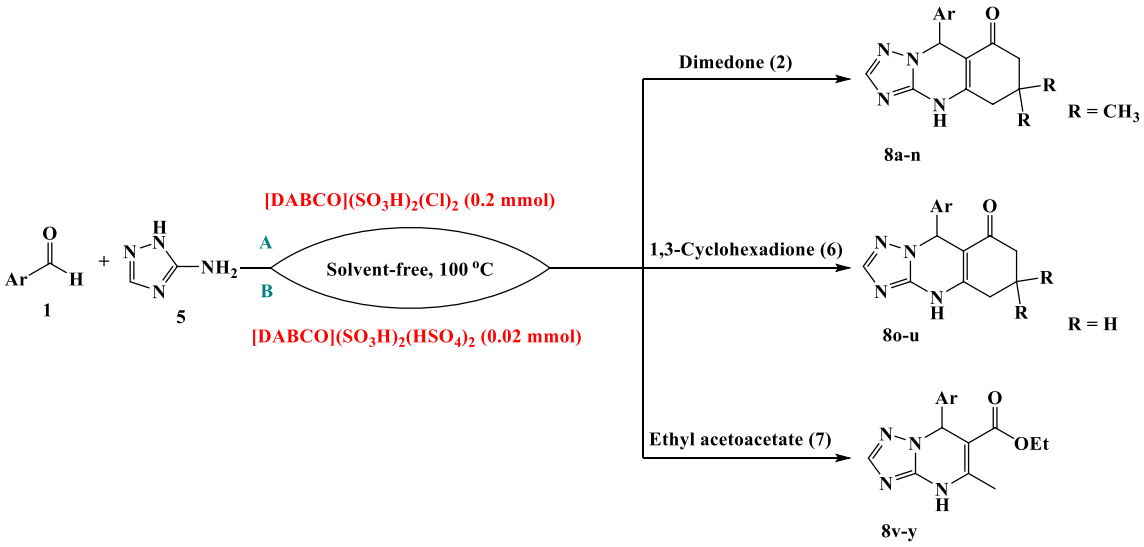
Table 1 Effect of temperature, amount of the catalyst and solvent in the synthesis of 12-(4-chlorophenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one **4b** ([DABCO]$(SO_3H)_2Cl_2$ and [DABCO]$(HSO_3)_2(HSO_4)_2$ are A and B, respectively)

Entry	Solvent	Condition/temperature (°C)	Catalyst (mmol)		Time (min)		Yield (%)	
			A	B	A	B	A	B
1	CH_2Cl_2	r. t.	0.14	0.04	180	180	Trace	Trace
2	CH_2Cl_2	Reflux	0.29	0.11	180	180	Trace	Trace
3	CH_3CN	r. t.	0.14	0.04	180	180	Trace	Trace
4	CH_3CN	Reflux	0.29	0.11	180	180	Trace	Trace
5	H_2O	50	0.14	0.04	180	180	Trace	Not complete
6	H_2O	Reflux	0.20	0.11	180	180	Trace	Not complete
7	EtOH: H_2O (1:1)	Reflux	0.20	0.04	180	180	Not complete	100 (70)[a]
8	EtOH	r. t.	0.20	0.04	150	130	100 (78)	100 (75)
9	EtOH	Reflux	0.20	0.04	120	105	100 (75)	100 (75)
10	–	Grinding/100 °C	0.20	0.04	90	70	100 (80)	100 (85)
11	–	100 °C	0.11	0.11	100	100	100 (87)	100 (85)
12	–	100 °C	0.20	0.02	75	60	100 (95)	100 (93)
13	–	100 °C	0.20	0.04	75	65	100 (93)	100 (93)
14	–	120 °C	0.20	0.02	75	60	100 (93)	100 (93)

[a] Isolated yield



Scheme 1 Synthesis of benzimidazoquinazolinone derivatives using [DABCO]$(SO_3H)_2Cl_2$ (method A) and [DABCO]$(HSO_3)_2(HSO_4)_2$ (method B)



Scheme 2 [DABCO]$(SO_3H)_2Cl_2$ (method A) and [DABCO]$(HSO_3)_2(HSO_4)_2$ (method B) catalyzed the synthesis of [1,2,4]triazolo/benzimidazolo quinazolinone and [1,2,4]triazolo[1,5-*a*]pyrimidine derivatives

Table 2 Preparation of triazolo/benzimidazoquinazolinone and triazolopyrimidine derivatives using [DABCO]$(SO_3H)_2Cl_2$ (method A) and [DABCO]$(HSO_3)_2(HSO_4)_2$ (method B) as the catalysts

Entry	Ar	Pro.	R	Amine	Time (min)		Yield (%)[a]		M. p. °C	
					A	B	A	B	Found	Rep. [References]
1	C_6H_5	4a	Me	3	80	75	90	90	>300	368 [19]
2	4-ClC_6H_4	4b	Me	3	75	60	95	93	>300	393 [19]
3	3-ClC_6H_4	4c	Me	3	80	65	90	87	>300	>300 [20]
4	2-ClC_6H_4	4d	Me	3	85	65	80	85	>300	>300 [20]
5	2,4-diClC_6H_3	4e	Me	3	105	85	90	90	>300	>300 [22]
6	4-BrC_6H_4	4f	Me	3	90	60	90	95	>300	369 [19]
7	4-FC_6H_4	4g	Me	3	80	65	85	90	>300	>300 [22]
8	4-$NO_2C_6H_4$	4h	Me	3	135	110	90	85	>300	335 [19]
9	3-$NO_2C_6H_4$	4i	Me	3	155	125	83	83	>300	>300 [20]
10	4-MeC_6H_4	4j	Me	3	120	90	87	90	>300	359 [19]
11	2-MeC_6H_4	4k	Me	3	100	90	80	80	>300	>300 [20]
12	4-$MeOC_6H_4$	4l	Me	3	130	100	87	85	>300	389 [19]
13	3-$MeOC_6H_4$	4m	Me	3	140	100	83	85	>300	>300 [20]
14	4-OHC_6H_4	4n	Me	3	165	120	90	90	>300	>300 [24]
15	4-$NMe_2C_6H_4$	4o	Me	3	180	135	80	78	>300	304–307 [29]
16	3-Indole-	4p	Me	3	175	120	80	75	>300	>300 [32]
17	C_6H_5	8a	Me	5	95	75	83	80	238–240	248–250 [16]
18	4-ClC_6H_4	8b	Me	5	65	60	90	93	295–297	303–305 [25]
19	2,4-diClC_6H_3	8c	Me	5	100	85	90	87	>300	323–325 [28]
20	4-BrC_6H_4	8d	Me	5	95	70	83	85	285–289	284–288 [25]
21	4-FC_6H_4	8e	Me	5	90	70	90	85	285–290	279–281 [26]
22	4-$NO_2C_6H_4$	8f	Me	5	125	100	90	80	290–294	284–285 [16]
23	3-$NO_2C_6H_4$	8g	Me	5	140	100	85	78	253–258	266–269 [24]
24	2-$NO_2C_6H_4$	8h	Me	5	140	120	80	75	283–285	290–292 [28]
25	4-MeC_6H_4	8i	Me	5	100	90	80	85	260–264	264–269 [25]
26	2-MeC_6H_4	8j	Me	5	105	85	85	81	295–299	>300 [20]
27	4-$MeOC_6H_4$	8k	Me	5	130	90	80	85	219–221	222–224 [16]
28	3-$MeOC_6H_4$	8l	Me	5	110	95	80	83	>300	>300 [20]
29	4-OHC_6H_4	8m	Me	5	135	120	85	90	>300	>300 [24]
30	2-Naphthyl	8n	Me	5	165	140	85	83	284–287	287–290 [24]
31	C_6H_5	8o	H	5	90	70	90	90	296–300	>300 [20]
32	4-ClC_6H_4	8p	H	5	90	75	90	90	294–296	— [27]
33	4-BrC_6H_4	8q	H	5	100	80	87	85	306–308	New
34	3-$NO_2C_6H_4$	8r	H	5	150	135	80	78	292–296	>300 [20]
35	2-$NO_2C_6H_4$	8s	H	5	150	130	80	80	300–304	New
36	4-MeC_6H_4	8t	H	5	120	90	80	83	>300	>300 [20]
37	4-$MeOC_6H_4$	8u	H	5	145	120	90	85	306–308	>300 [20]
38	C_6H_5	8v	EAA[b]	5	100	90	83	85	191–192	190–192 [26]
39	4-$NO_2C_6H_4$	8w	EAA	5	120	100	80	80	255–259	263–264 [26]
40	4-MeC_6H_4	8x	EAA	5	105	75	85	78	237–241	246–248 [26]
41	4-$MeOC_6H_4$	8y	EAA	5	120	80	80	75	232–236	220–223 [26]

[a] Isolated yields

[b] Ethyl acetoacetate

$[DABCO](SO_3H)_2(HSO_4)_2$ (method B) was selected as a model system. As presented in Table 1, among tested solvents in different conditions the best result that was obtained under solvent-free condition at 100 °C (method B) was selected as a model system. As presented in Table 1, among tested solvents in different conditions the best result was obtained under solvent-free condition at 100 °C (Scheme 1).

Afterward and on the basis of the above-mentioned results, we also utilized the optimized conditions for the synthesis of triazoloquinazolinone and triazolopyrimidine derivatives by replacing 3-amino-1,2,4-triazole with 2-aminobenzimidazole using a variety of β-diketones as represented in Scheme 2.

Therefore, different derivatives of the stated compounds were prepared with different aromatic aldehydes and the outcomes are listed in Table 2. The time of the reaction was within 75–180 min for $[DABCO](SO_3H)_2Cl_2$ (method A) and 60–140 min for $[DABCO](HSO_3)_2(HSO_4)_2$ (method B), and high yields of [1,2,4]triazolo/benzimidazolo quinazolinones and [1,2,4]triazolo[1,5-*a*]pyrimidines were attained in the presence of both of the catalysts.

It is worthwhile and eco-friendly that a catalyst could be recyclable. For this reason, we chose a model reaction to investigate the reusability of both of the catalysts. Synthesis of 12-(4-chlorophenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo [4, 5] imidazo[2,1-*b*]quinazolin-1(2*H*)-one **4b** was tested under the optimized reaction conditions using $[DABCO](SO_3H)_2Cl_2$ (method A) and $[DABCO](HSO_3)_2(HSO_4)_2$ (method B), respectively. After completion of the reaction, the solid product was washed with water to separate the catalyst. Then, the filtrate was evaporated under vacuum up to 70 °C, and the obtained catalyst was washed with diethyl ether, dried and reused at least for the same reaction. The recycled reagents were reused for three runs with only the modest

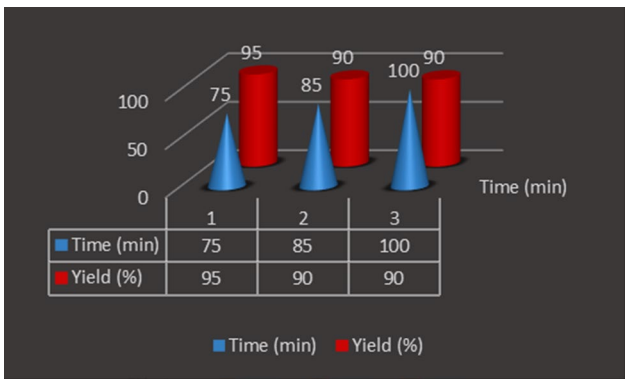


Fig. 2 Reusability of $[DABCO](HSO_3)_2(Cl)_2$ in the synthesis of 12-(4-chlorophenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo[4, 5]imidazo [2,1-*b*]quinazolin-1(2*H*)-one **4b**

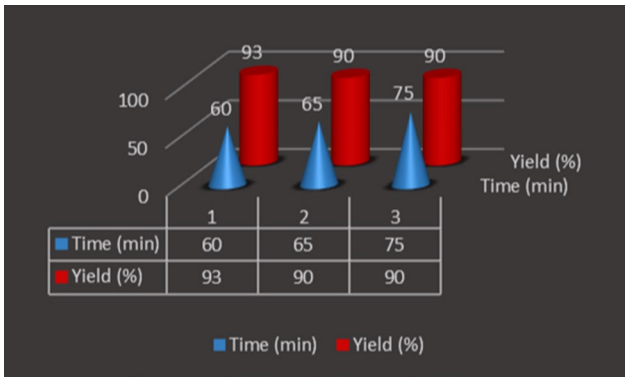


Fig. 3 Reusability of $[DABCO](HSO_3)_2(HSO_4)_2$ in the synthesis of 12-(4-chlorophenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo[4,5] imidazo[2,1-*b*]quinazolin-1(2*H*)-one **4b**

loss of efficiency. The obtained results are demonstrated in Figs. 2 and 3.

To compare the efficiency of $[DABCO](HSO_3)_2(Cl)_2$ and $[DABCO](HSO_3)_2(HSO_4)_2$ in Table 3, the reaction times, yields and amounts of the catalysts in the synthesis of **4a**, **8a**, **8o** and **8v** are compared with other previous procedures. The comparative results showed that the synthesis of these compounds in the presence of $[DABCO](HSO_3)_2(Cl)_2$ and $[DABCO](HSO_3)_2(HSO_4)_2$ is carried out in good times and yields and lowest amount of the catalyst; moreover, use of extra amount of substrates was prevented, which was why this procedure became affordable.

Based on our observations and according to the previous reports, a possible mechanism for the synthesis of quinazolinone derivatives is shown in Scheme 3. At the first step, a Knoevenagel condensation occurs between activated aldehyde **a** and enol **c** to prepare intermediate **d**. After this step, the reaction can accomplish in two routes (**I, II**). If intermediate **d** loses water, route **I** can take place producing α,β-unsaturated carbonyl compound **e**. Then, Michael addition reaction of nitrogen number **2** in amine **5** makes intermediate **f**. An intra-molecular cyclization in **f** happens, and it loses water to produce observed quinazolinone **8**. This reaction can follow through route **II**, if the carbonyl group in **d** activated by H from the ionic liquid. Difference between routes **I** and **II** is in the initial attack of the nitrogen atom of amine. In route **II**, amino group instead of N^2 engages in reaction. The intermediate **h** undergoes intramolecular cyclization to give the desired products [30–32].

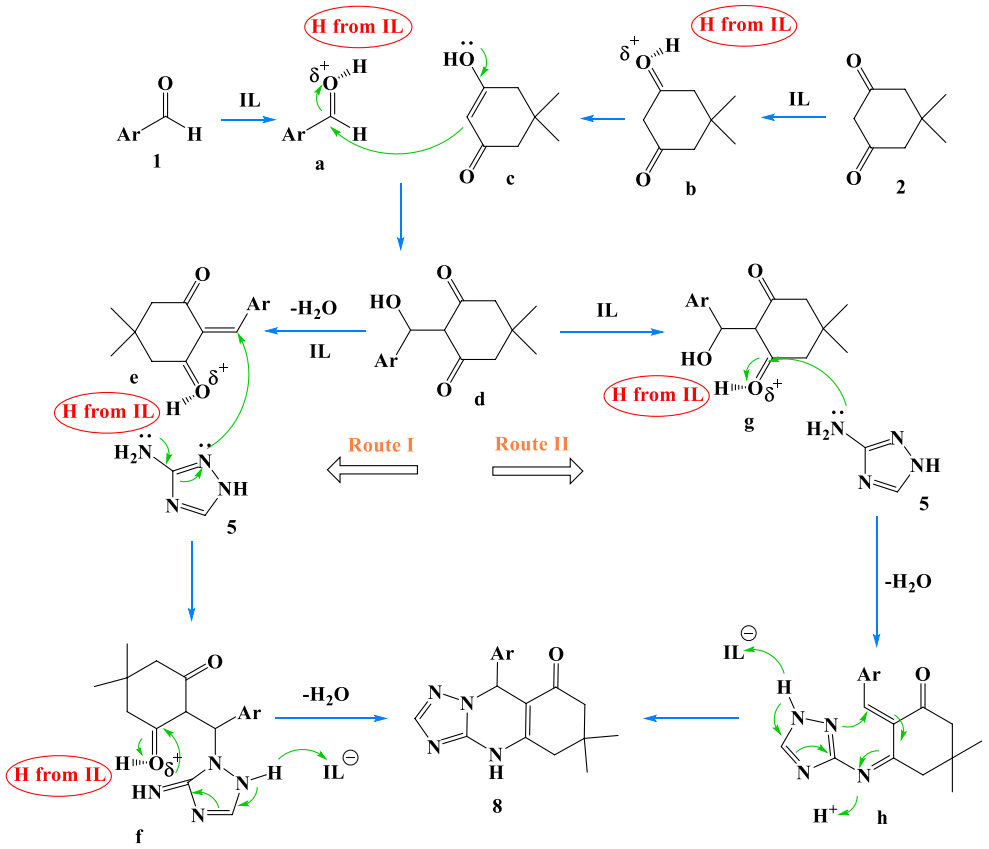
As shown in Scheme 3, during the reaction, both DABCO-based ionic liquids participated in the reaction by producing H^+ in medium. H^+ was consumed and produced repeatedly until the reaction was completed, and ultimately, ILs were separated by workup procedure without consuming.

Table 3 Compared performance of various catalysts with $[DABCO](HSO_3)_2(Cl)_2$ and $[DABCO](HSO_3)_2(HSO_4)_2$ in the synthesis of quinazolinone derivatives (**4a**, entries 1–16; **8a**, entries 17–30; 8o, entries 31–34; 8v, entries 35–38)

Entry	Catalyst/amount (mol%)	Conditions	Time (min)	Yield (%)[a]	TOF (min^{-1})	References
1	–	DMF/reflux	5	65	–	[15]
2	–	EtOH/reflux	90	64	–	[18]
3	–	Solvent free/110 °C	420	85	–[b]	[20]
4	–	H_2O/MW	4	93	–	[22]
5	Silica gel	MW (150 W)/120 °C	3	95	–	[23]
6	$H_6P_2W_{18}O_{62}.H_2O$/1	CH_3CN/Reflux	15	96	640	[24]
7	Sulfamic acid/0.005	CH_3CN/80 °C	15	94	125,333.3	[25]
8	[Bmim]Br/0.1	Solvent free/100 °C	5	94	18800	[27]
9	Iodine/10	CH_3CN/Reflux	10	84	84	[28]
10	Fe_3O_4@chitosan/2 (mg $mmol^{-1}$)	EtOH/40 °C	90	90	–	[29]
11	*p*-Toluenesulfonic acid/15	CH_3CN/40–50 °C	25	95	25.33	[30]
12	Acetic acid/8.7	Solvent free/60 °C	20	94	54.02	[31]
13	Nano-SiO_2/15	CH_3CN, r.t.	25	95	25.33	[32]
14	SBA–Pr–SO_3H/0.05 (g)	Solvent free/100 °C	10	90	–	[33]
15	Fe_3O_4@clay/5 (mg)	H_2O/r.t.	12	94	–	[56]
16	$[DABCO](HSO_3)_2(Cl)_2$/0.02	Solvent free/100 °C	80	90	5625	This work
17	$[DABCO](HSO_3)_2(HSO_4)_2$/0.002	Solvent free/100 °C	75	90	60,000	This work
18	–	DMF/reflux	30	76	–	[16]
19	–	Solvent free/110 °C	240	93	–[b]	[20]
20	Silica gel	MW (150 W)/120 °C	4	90	–	[23]
21	$H_6P_2W_{18}O_{62}.H_2O$/1	CH_3CN/reflux	30	95	316.67	[24]
22	Sulfamic acid/0.005	CH_3CN/80 °C	30	95	633,333.3	[25]
23	$[Bmim]BF_4$/15	Grinding/r. t.	11	92	55.76	[26]
24	[Bmim]Br/0.1	Solvent free/100 °C	20	93	4650	[27]
25	Iodine/10	CH_3CN/reflux	10	81	81	[28]
26	*p*-Toluenesulfonic acid/15	CH_3CN/40–50 °C	30	96	21.33	[30]
27	Acetic acid/8.7	Solvent free/60 °C	25	95	43.68	[31]
28	Nano-SiO_2/15	CH_3CN, r.t.	30	96	21.33	[32]
29	SBA–Pr–SO_3H (0.05 g)	Solvent free/100 °C	5	90	–	[33]
30	$[DABCO](HSO_3)_2(Cl)_2$/0.02	Solvent free/100 °C	95	83	4368.42	This work
31	$[DABCO](HSO_3)_2(HSO_4)_2$/0.002	Solvent free/100 °C	75	80	53,333.3	This work
32	–	Solvent free/110 °C	240	90	–[b]	[20]
33	[Bmim]Br/0.1	Solvent free/100 °C	30	90	3000	[27]
34	$[DABCO](HSO_3)_2(Cl)_2$/0.02	Solvent free/100 °C	90	90	5000	This work
35	$[DABCO](HSO_3)_2(HSO_4)_2$/0.002	Solvent free/100 °C	70	90	45,000	This work
36	HCl/1–2 drops	EtOH/reflux	420	56	–	[18]
37	$[Bmim]BF_4$/15	Grinding/r. t.	12	80	44.44	[26]
38	$[DABCO](HSO_3)_2(Cl)_2$/0.02	Solvent free/100 °C	100	83	4150	This work
39	$[DABCO](HSO_3)_2(HSO_4)_2$/0.002	Solvent free/100 °C	90	85	47,222.2	This work

[a] Isolated yields

[b] In this procedure, aldehyde (3 mol), *β*-diketones (1 mol) and 2-aminobenzimidazole/3-amino-1,2,4-triazole (1.1 mol) were used



Scheme 3 Proposed mechanism for the synthesis of quinazolinone derivatives in the presence of $[DABCO](HSO_3)_2Cl_2$ and $[DABCO](HSO_3)_2(HSO_4)_2$

Conclusions

In conclusion, in this study two efficient and environmentally benign ionic liquids, $[DABCO](HSO_3)_2(Cl)_2$ and $[DABCO](HSO_3)_2(HSO_4)_2$, were utilized for the synthesis of different types of quinazolinone derivatives. These reagents are green, easy to prepare and inexpensive catalysts that can accelerate the synthesis of triazoloquinazolinone and benzimidazoquinazolinones through a simple procedure from aromatic aldehydes, varied *β*-diketones and 2-aminobenzimidazole/3-amino-1,2,4-triazole; besides, [1,2,4]triazolo[1,5-*a*] pyrimidines derivatives were synthesized in this procedure by using ethyl acetoacetate. After completion of the reaction, use of extra amount of substrates and any solvent was prevented. The applied methods show some advantages including operational simplicity, high yields, no by-products and easy workup due to no need of column chromatography for isolation. On the other hand, applied conditions for the preparation of the catalysts and quinazolinone derivatives are kinder and milder than available methods.

Acknowledgements We are thankful to the University of Guilan Research Council for the partial support of this work.

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