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One-pot synthesis of pyrimido[4,5-*d*]pyrimidine derivatives using a new DABCO-based ionic liquid catalyst

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Original Research

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Abstract:

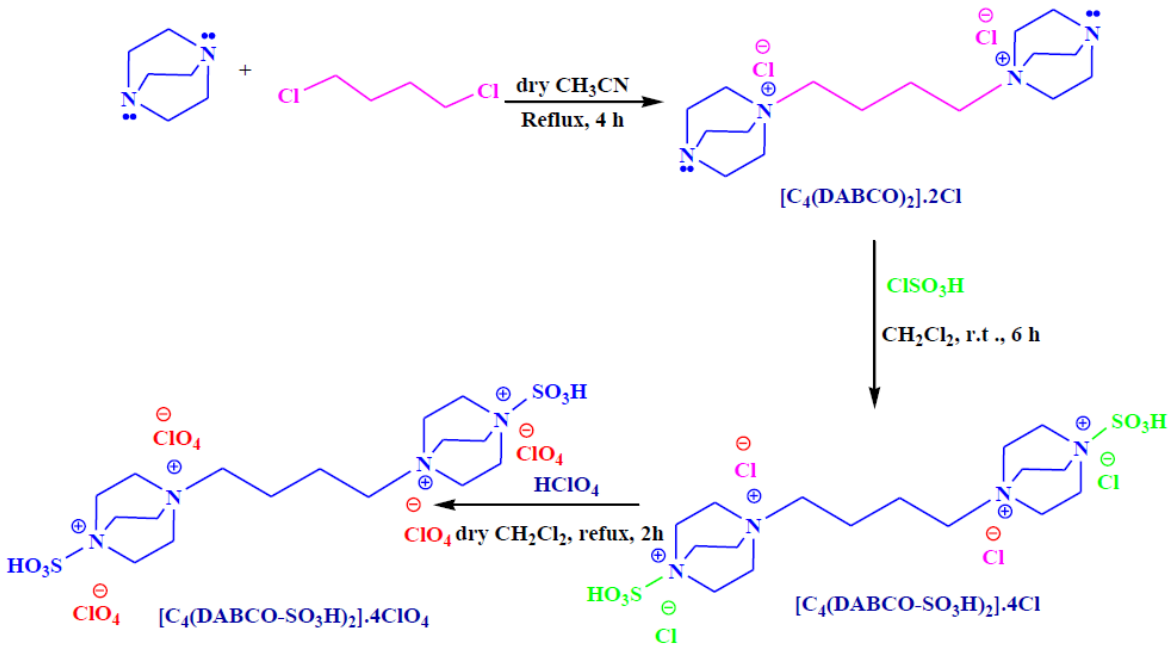
In this research, an efficient one-pot synthesis of pyrimido[4,5-*d*]pyrimidine derivatives has been described using a new DABCO-based ionic liquid catalyst formulated as $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$. Some of the important features of the reported method are short reaction times, easy work-up and isolation of the products from the reaction media, high yields and reusability of the catalyst.

Keywords: DABCO; Heterocyclic compound; Ionic liquid; Pyrimido[4,5-*d*]pyrimidines; $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$

1. Introduction

In the last decades, the synthesis of heterocyclic compounds, as one of the largest classes of organic constitute, has attracted considerable attention from many organic chemists. This is because the heterocyclic compounds are known to demonstrate a wide range of important pharmacological activities [1–4]. Among these compounds, pyrimidine derivatives, the well-known class of organic compounds, show different biological and pharmaceutical activities such as PI3K/mTOR dual inhibitors [5], potent inhibitory activity on EGFR, and the highest cytotoxicity against MCF7 and MDA-MB-361 [6]. These compounds also are able to represent anticancer, anti-infectious, anti-diabetic, antioxidant, RIPK3-Mediated necroptosis inhibitors, antimicrobial, and antitumor activities [7–12]. Based on the mentioned important characteristics to accelerate the synthesis of these compounds, a variety of catalysts have been reported in the literature, which of them Mn-ZIF-8@$ZnTiO_3$ nanocatalyst [13], iodine [14], PANI-Fe_3O_4@ZnO nanocomposite [15], magnetic Fe_3O_4 nanoparticles in the melamine-based ternary deep eutectic solvent [16], *p*-toluenesulfonic acid [17], triethylammonium hydrogen sulfate $[Et_3NH][HSO_4]$ [18], $CuCl_2$, K_2CO_3 [19], $NbCl_5$ [20], nano Fe_3O_4 [21], UO_2 $(NO_3)_2.6H_2O$ [22], *L*-proline [23], and CH_3COOH [24] are examples.

Ionic liquids (ILs) are considered potent green solvents in supersede to volatile organic solvents. ILs dominate low vapor pressure, low viscosity, non-volatility under ambient conditions, good solubility, acidity or basicity, and long-range thermal stability [25, 26]. So, these unique properties attracted the attention of many researchers who wanted to study their utilization in free or supported form, and many reports have been published in this field. Some of these reports are about the use of aprotic ILs [27], hydrophilic poly(ethylene glycol)-ionic liquid [28], g-C_3N_4-SO_3H nanosheet IL [29], poly(ionic liquid)–covalent organic framework hybrids [30], Bronsted acidic ionic liquids [31], Ag–Pd nanoparticles supported on SBA silica through [DMAP-TMSP-DABCO]OH basic ionic liquid [32], nano ionic liquid 1-methylimidazolium trinitromethanide $[HMIM]C(NO_2)_3$ [33], etc. In addition, there



Scheme 1. Preparation of $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$.

have been many applications in the use of ILs in industry, including catalysis [34–36], biodiesel production [37, 38], operating fluids instead of solvents [39], stationary phases in gas chromatography (GC) columns [40], and electrochemistry [41, 42].

In this study, and in continuation of our interest in the introduction of ionic liquid catalysts for the synthesis of heterocyclic compounds [43–46], we wish to report the efficient applicability of a newly reported ionic liquid $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ [47] in the acceleration of the synthesis of pyrimido[4,5-*d*]pyrimidine derivatives.

2. Experimental

All solvents and chemical materials were purchased from Fluka, Merck, and Aldrich Chemical Companies and used without further purification. The reaction progress was followed by TLC on silicagel Polygram SILG/UV 254 plates. Products were characterized by their physical properties and spectral data. Melting points were measured by an Electro-Thermal IA 9100 melting point apparatus. Perkin-Elmer spectrum BX series spectrophotometer was used for the recording of Fourier transform infrared (FT-IR) spectra of the samples using potassium bromide pellets in the range of 400-4000 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded using a Bruker Advance DRX-300 MHz instrument. In this method, TMS was used as an internal standard in DMSO.

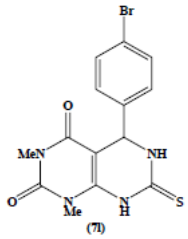
-Preparation of 1,1'-(butane-1,4-diyl)-bis(1,4-diazabicyclo [2.2.2]octane-1-ium)tetraper chlorate[$C_4(DABCOSO_3H)_2$]. $4ClO_4$

At first, A mixture of 1,4-dichlorobutane (0.547 mL, 5 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.121 g, 10 mmol) in dry acetonitrile (25 mL) was refluxed for 4 h. After cooling to room temperature, the solid product was filtered, washed with diethyl ether repeatedly (3×5 mL) and dried under vacuum to give 1,1'-(butane-1,4-diyl)-bis-(1,4-diazabicyclo[2.2.2]octane-1-ium)chloride ($[C_4(DABCO)_2].2Cl$) as a white solid. Then, a stoichiometric amount of chlorosulfonic acid (0.66 mL, 10 mmol) was added drop-wise to a mixture of the obtained solid in dry CH_2Cl_2 (25 mL) in an ice bath. After the addition was completed, the flask was stirred at room temperature for 6 h. Then, the solid product was washed with diethyl ether repeatedly (3 × 5 mL) and dried under vacuum to give 4,4'-(butane-1,4-diyl)-bis(1-sulfo,1,4-diazabicyclo[2.2.2]octane-1-ium)tetrachloride ($NS\text{-}[C_4(DABCO\text{-}SO_3H)_2.4Cl$) as a yellow solid. Finally, a mixture of these solids (2.73 g, 10 mmol) in dry CH_2Cl_2 (25 mL) was prepared, and perchloric acid (0.85 mL, 10 mmol) was added drop-wise to it over a period of 30 min in an ice bath. After the addition was completed, the reaction mixture was refluxed for 2 h. After all, the obtained products were dried under vacuum to achieve $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ (Scheme 1).

General procedure for the synthesis of pyrimido[4,5-d] pyrimidine derivatives

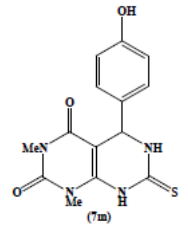
A mixture of the selected aromatic aldehyde **1** (1 mmol), 6-amino-1,3-dimethyluracil **2** (1 mmol) or barbituric acid **3** (1 mmol) and urea **4** or thiourea **5** (1 mmol) was stirred at room temperature in the presence of $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ (5.2% mol). The reaction process was followed by TLC [*n*-Hexane: ethylacetate: MeOH (7:3:1)]. Upon completion, the mixture was filtered off, and the residue was washed with water several times. The obtained product was recrystallized from ethanol to obtain the pure product **(6a-n or 7a-n)**.

The spectral data of the new compounds are as follows:



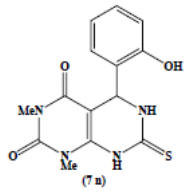
(7l)

5,6,7,8-Tetrahydro-5-(4-bromophenyl)-1,3-dimethyl-7-thioxopyrimido[4,5-*d*]pyrimidine-2,4(1*H*,3*H*)-dione. White powder, M.p > 300 °C; FT-IR (KBr, cm^{-1}) υ_{max}: 3057, 2817, 1578, 1372, 1044; ^{1}H NMR (300 MHz, DMSO-*d6*) δ (ppm): 3.29 (s, 6H, CH_3), 5.60 (s, 1H), 6.84-7.12 (m, 4H), 9.40 (s, 1H, NH), 10.21 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 30.4, 31.0, 44.2, 83.9, 116.0, 126.0, 128.5, 130.2, 131.6, 151.6, 156.1, 157.9, 162.1, 192.6.



(7m)

5,6,7,8-Tetrahydro-5-(4-hydroxyphenyl)-1,3-dimethyl-7-thioxopyrimido[4,5-*d*]pyrimidine-2,4(1*H*,3*H*)-dione. Cream powder, M.p > 300 °C; FT-IR (KBr, cm^{-1}) υ_{max}: 3484, 3200, 3050, 2817, 1675, 1641, 1597, 1504; ^{1}H NMR (300 MHz, DMSO-*d6*) δ (ppm): 3.22 (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 5.51 (s, 1H), 6.87-6.93 (m, 4H), 9.03 (s, 1H, NH), 9.80 (s, 1H, NH), 10.87 (s, 1H, OH); ^{13}C NMR (75 MHz, DMSO-*d6*) δ (ppm) 29.1, 32.8, 43.9, 84.7, 119.4, 125.6, 129.6, 135.1, 156.2, 157.3, 160.3, 192.5.



(7 n)

5,6,7,8-Tetrahydro-5-(2-hydroxyphenyl)-1,3-dimethyl-7-thioxopyrimido[4,5-*d*]pyrimidine-2,4(1*H*,3*H*)-dione Yellow powder, M.p > 300 °C; FT-IR (KBr, cm^{-1}) υ_{max}: 3290, 3043, 2816, 1647, 1556, 1463; ^{1}H NMR (300 MHz, DMSO-*d6*) δ 3.21 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 5.17 (s, 1H), 7.00-7.60 (m, 4H), 8.27 (s, 1H), 10.19 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d6*) δ (ppm) 28.4, 29.1, 42.3, 82.6, 116.0, 124.3, 127.9, 129.8, 132.6, 150.9, 155.1, 156.8, 161.3, 191.4.

3. Results and discussion

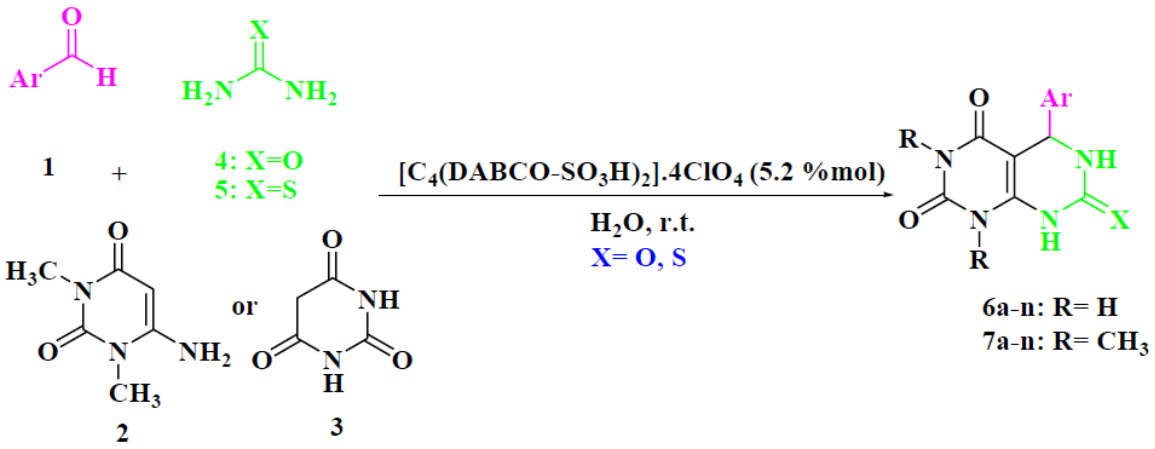
The first step of this study was the optimization of the reaction conditions. For this purpose the reaction between 4-chloro benzaldehyde (1 mmol), 6-amino-1, 3-dimethyluracil (1 mmol) and urea (1 mmol) was selected as a model system and the effect of various amounts of the catalyst in the presence and absence of solvent at a variety of temperatures was investigated on it. The results are tabulated in the Table. 1.

This table shows that the use of 5.2% mol of $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ in H_2O as the solvent at room temperature can lead to higher yields in lower times (Entry 3) (Scheme 2). After the optimization studies and in order to clarify the generality of the selected method, different aromatic aldehydes, containing both electron-donating and electron-withdrawing groups, were used to prepare their corresponding pyrimido[4,5-*d*] pyrimidine derivatives under the same conditions. The obtained results show that using this method, all the products can be obtained in a short time with high isolated yields (Table. 2). It is important to note that under the selected conditions, the kind of the substituent and its position on the aromatic ring and also use of thio urea instead of urea has no significant effect on the obtained results. The proposed mechanisms of these reactions are shown in Scheme 3. As shown in Scheme 3, the prepared $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ ionic liquid can activate the carbonyl groups and accelerate the enolization. In route 2, the enolized 1,3-diketone (2 or 3) moiety attacks the carbonyl group of the aldehyde, and this is followed by the elimination of a molecule of water. Then urea (thiourea) takes part in a Michael addition with intermediate B to convert to intermediate C. Finally, an intra-molecular cyclization and loss of water cause the production of the requested product in route 1, urea (or thiourea) attacks to activate aldehyde by the electron-lone pairs of nitrogen to prepare intermediate A. Then 1,3-diketone (2 or 3) was combined with it to change into intermediate C. Consequently, the

Table 1. The effect of various conditions in the synthesis of pyrimido[4,5-d] pyrimidine **6d**.

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (min.)	Yield (%)[a]
1	-	-	25	60	Trace
2	4.2	H_2O	25	60	62
3	5.2	H_2O	25	10	96
4	5.2	$CHCl_3$	reflux	60	Trace
5	5.2	CH_3CN	reflux	60	Trace
6	5.2	EtOH	reflux	60	60
7	5.2	EtOH/H_2O (1:1)	reflux	60	70

[a] Isolated yields.



Scheme 2. Synthesis of pyrimido[4,5-*d*] pyrimidine derivatives in the presence of $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$.

product was produced by an intra-molecular cyclization in intermediate I and loss of water.

At the next step of the study and in order to stablish the reusability of $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$, after the completion of the model reaction. For this purpose, the reaction mixture was filtered off after completion of the reaction. Then the recovered catalyst was attained by evaporating the solvent under vacuum up to 70 °C. Next, the obtained residue was washed with diethyl ether and reused for new reactions. The results showed that this catalyst can be reused at least five times in the synthesis of pyrimido[4,5-*d*] pyrimidine derivatives without the significant loss of its catalytic activity (Figure. 1). The similarity of the FT-IR spectra of the reused and the freshly prepared catalyst confirms its

Table 2. Synthesis of pyrimido[4,5-*d*] pyrimidine using $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ as the catalyst.

Entry	Aldehyde	X	Product	Yield (%)[a]	m. p. (°C) Observed	Reported [48–50]
1	C_6H_5CHO	O	6a	92	241-243	**240-244**
2	4-BrC_6H_4CHO	O	6b	95	212-214	**210-214**
3	3-$NO_2C_6H_4CHO$	O	6c	93	200-202	**200-203**
4	4-ClC_6H_4CHO	O	6d	96	296-298	**296-298**
5	4-MeC_6H_4CHO	O	6e	90	246-247	**246-247**
6	4-$OMeC_6H_4CHO$	O	6f	89	241-243	**246-247**
7	4-$NO_2C_6H_4CHO$	O	6g	96	241-243	**246-247**
8	4-OHC_6H_4CHO	O	6h	87	> 300	> **300**
9	2-OHC_6H_4CHO	O	6i	87	262-264	**262-264**
10	3-$NO_2C_6H_4CHO$	S	6j	94	180-182	**180-185**
11	C_6H_5CHO	S	6k	91	285-286	**285-287**
12	4-ClC_6H_4CHO	S	6l	93	278-279	**278**
13	4-MeC_6H_4CHO	S	6m	90	> 300	> **300**
14	4-$OMeC_6H_4CHO$	S	6n	88	> 300	> **300**
15	4-$NMe_2C_6H_4CHO$	O	6o	91	251-253	**250-254**
16	4-BrC_6H_4CHO	O	7a	94	> 300	**307**
17	3-$NO_2C_6H_4CHO$	O	7b	92	200-202	**200-202**
18	4-ClC_6H_4CHO	O	7c	95	> 300	**312**
19	4-MeC_6H_4CHO	O	7d	91	> 300	**315**
20	4-$OMeC_6H_4CHO$	O	7e	90	> 300	**307**
21	C_6H_4CHO	O	7f	91	244-246	**244-246**
22	4-FC_6H_4CHO	O	7g	89	> 300	**244-246**
23	C_6H_4CHO	S	7h	90	256-258	**308**
24	4-ClC_6H_4CHO	S	7i	94	> 300	**257-259**
25	4-MeC_6H_4CHO	S	7j	89	> 300	> **300**
26	3-BrC_6H_4CHO	O	7k	94	> 300	> **300**
27	3-BrC_6H_4CHO	S	7l	92	> 300	**New**
28	4-OHC_6H_4CHO	S	7m	90	> 300	**New**
29	2-OHC_6H_4CHO	S	7n	89	> 300	**New**

[a] Isolated yields.

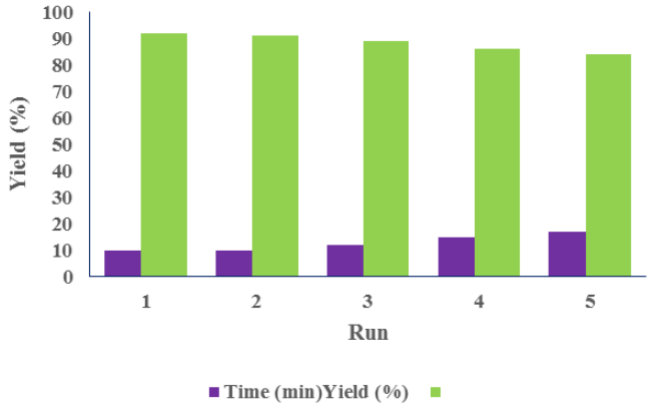
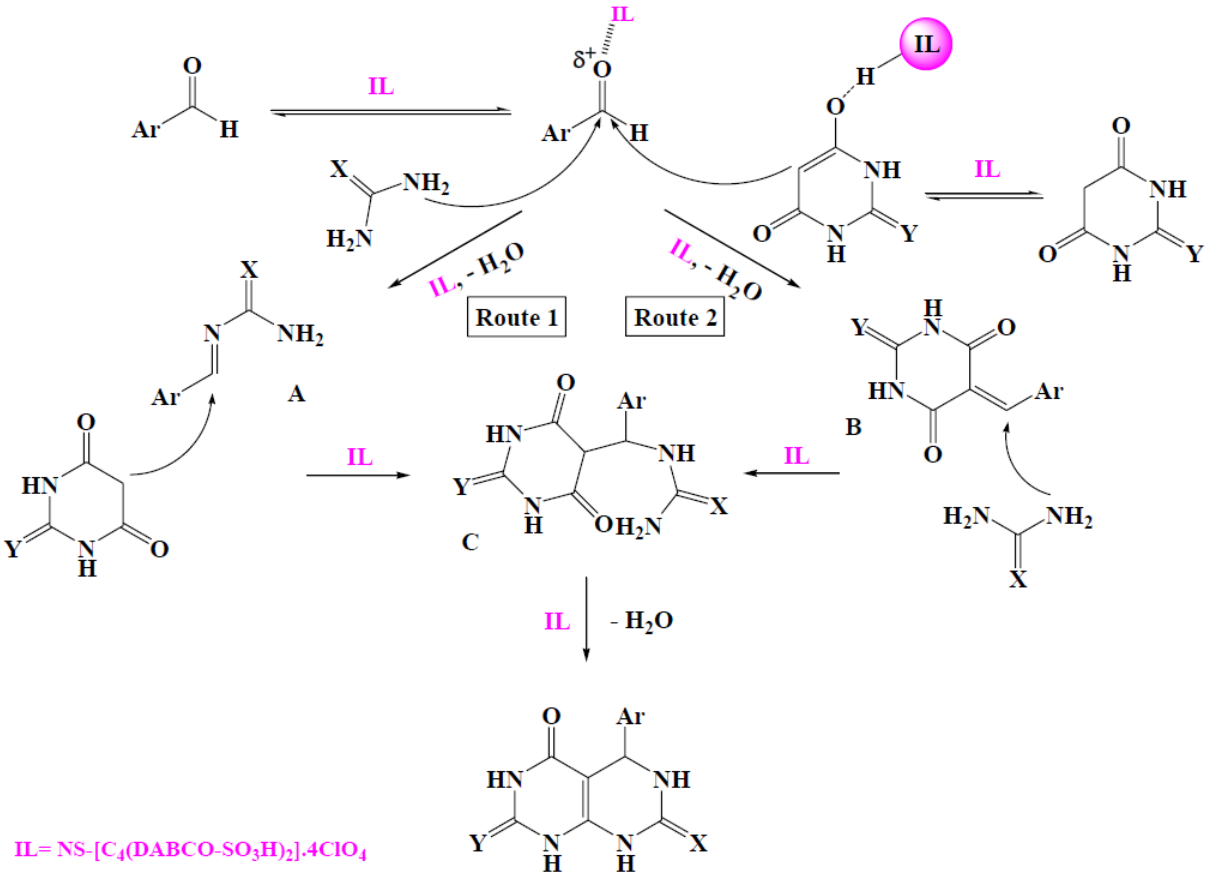


Figure 1. Reusability of $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ in the synthesis of **6d**.



Scheme 3. The proposed mechanism of the synthesis of pyrimido[4,5-*d*] pyrimidine by $[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$.

Table 3. Comparison of the obtained results in the synthesis of **6d** in the presence of NS-$[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$ with some of those reported in the literature.

Entry	Catalyst	Amount (mol)	Conditions	Time (min.)	Yield (%)	TOF (s^{-1})	Ref.
1	$[H_2\text{-DABCO}][ClO_4]_2$	1.3×10^{-4}	H_2O/75 °C	20	92	589.7	48
2	*L*-Proline	0.05	MW/450W	13	76	1.95	23
3	-	-	Water/MW/560W	180	86	-	49
4	Ceric Ammonium Nitrate (CAN)	1.0×10^{-4}	H_2O/reflux	20	98	816.7	50
5	$[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$	5.2×10^{-5}	H_2O/r.t.	10	96	3076	This study

stability under the selected reaction conditions.
Comparison between the results obtained for the synthesis of pyrimido[4,5-*d*]pyrimidine derivatives using the present method and some of the previously reported ones clearly clarifies the merit of $[C_4(DABCO\text{-}SO_3H)_2].{}_4ClO_4$ in terms of the amount of the catalyst, reaction times and yields, and turn over frequency (TOF) (Table. 3).

4. Conclusion

In conclusion, in this study a newly reported DABCO-based acidic ionic liquid ($[C_4(DABCO\text{-}SO_3H)_2].4ClO_4$) was used for the acceleration of the synthesis of pyrimido[4,5-*d*] pyrimidine derivatives *via* one-pot three component condensation reactions. The mentioned method shows some advantages such as high yields, no by-products, and easy work-up, use of non-expensive materials, not using hazardous organic solvents, and use of a reusable catalyst.

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Authors Contributions
All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Sanaz Sahrapeyma and Farhad Shirini. The first draft of the manuscript was written by Sanaz Sahrapeyma, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Availability of Data and Materials
All data generated or analyzed during this study are included in this published article.

Conflict of Interests
The authors declare that they have no competing interests.

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