Journal of the Iranian Chemical Society
https://doi.org/10.1007/s13738-021-02177-0

ORIGINAL PAPER

Introduction of bis-imidazolium dihydrogen phosphate as a new green acidic ionic liquid catalyst in the synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran derivatives

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Received: 8 September 2020 / Accepted: 5 January 2021

Abstract
In this work, $[H_2\text{-Bisim}][H_2PO_4]_2$ as a novel bis-imidazole-based acidic ionic liquid has been synthesized and characterized with a variety of techniques including FT-IR, ^1H, ^{13}C, ^{31}P NMR and mass spectroscopy techniques. After characterization, this compound was used as an affordable and recyclable catalyst in the synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran derivatives. The procedure had several advantages such as excellent yields, short reaction times, simple workup and use of a non-expensive and non-toxic compound as the catalyst. Moreover, the prepared ionic liquid could be recycled and reused without significant loss in its catalytic activity in the studied reactions.

Keywords Bis-imidazole · Ionic liquids · Arylidene malononitrile · $[H_2\text{-bisim}][h_2PO_4]_2$ · Ethyl(*E*)-3-(aryl)-2-cyanoacrylate · Tetrahydrobenzo[*b*]pyran

Introduction

In the last few decades, ionic liquids (ILs) have attracted increasing interests of organic chemists, because of their unique properties such as nonflammability, negligible vapor pressure, high thermal, chemical and electrochemical stability, and also reusability [1–3]. Because of these important characteristics, these types of compounds were widely used in approximately all fields of chemistry such as Li-ion batteries [4] synthesis [5], electrochemistry [6], catalysis [7–9], extraction and chromatography [10].

Multi-component reactions (MCRs) have appeared as an efficient and important tool in modern synthetic organic chemistry because of the ability to produce the designed compounds with high atom economy, low costs and excellent yields by the reaction of three or more compounds together in one step. MCRs have been mostly utilized in the synthesis of natural products and other biologically active molecules, so they have played a vital role in the development of synthetic pharmaceutical chemistry. Besides, MCRs contribute to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption and waste production, and also increase the simplicity of extraction and purification processes [11].

The Knoevenagel condensation is a considerable reaction for the formation of C=C bonds from a carbonyl compound and a compound containing an active methylene group [12]. This reaction is one of the most important methods to obtain natural products [13], herbicides [14] polymers [15], perfumes, cosmetics [16] and several therapeutic drugs [17], such as epalrestat [18] and atorvastatin [19]. Throughout the years, various methods and catalysts were reported for Knoevenagel condensation, which of them metal–organic frameworks (MOFs) [20–22], CTMAB [23], NAP-SiO_2 [24], porous calcium hydroxyapatite [25], Citrus limonum [26],

Supplementary Information The online version of this article (https://doi.org/10.1007/s13738-021-02177-0) contains supplementary material, which is available to authorized users.

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Published online: 25 January 2021

SiO_2-*L*-proline [27], MgO/ZrO_2 [28], mpg-C_3N_4-tBu [29], amino-functionalized mesoporous silica [30], carbon-doped hexagonal boron nitride (BCN) [31], graphene oxide (GO) [32], mesoporous titanosilicate Ti-TUD-1 [33], Taurine [34], onion elixir [35] and γ-Fe_2O_3@SiO_2@[Bis-APTES]Cl_2 NPs [36] [DABCO-PDO][CH_3COO][37], Mn(III)–pentadentate Schiff base [38] [H_2-DABCO][H_2PO_4]$_2$ [39] and nano-α-Al_2O_3 [40] are the examples.

Recently, benzopyran scaffolds have been interested in their diverse biological potentials such as anticancer [41], antioxidant [42], antimicrobial [43]. Several methods have been reported for the synthesis of tetrahydrobenzo[*b*] pyran derivatives, using a variety of catalysts and reagents, such as Taurine [34], *p*-Dodecylbenzenesulfonic acid (DBSA) [44], 2,2,2-trifluoroethanol [45], $PhB(OH)_2$ [46], $Ce1Mg_{0\cdot6}Zr_{0\cdot4}O_2$ [47], DABCO [48], dihydrogen phosphate supported silica-coated magnetite nanoparticles (H_2PO_4-SCMNPs) [49], hexadecyldimethyl benzyl ammonium bromide (HDMBAB) [50], [TEBSA].HSO_4 [51], *L*-pyrrolidine 2-carboxylic acid sulfate (LPCAS) [52], Na_2SeO_4 [53] and nano-ZnO [54].

Although the methods which have been reported for the promotion of the above-mentioned target molecules lead to considerable enhancements, some of them suffer from disadvantages such as long reaction times, low yields and harsh reaction conditions. Therefore, the introduction of efficient and economical catalysts that can solve these issues are still in demand.

Experimental

Materials and instruments

All chemicals such as solvents, aldehydes, dimedone, cyclohexanedione, malononitrile and ethyl cyanoacetate were purchased from Merck Chemical Company (Munich) and were used without further purification. The progress of the reaction was monitored by thin layer chromatography (TLC).

Products were characterized by their physical constants, comparison with authentic samples by their FT-IR and melting points. The purity determination of the substrate and reaction monitoring was accomplished by TLC on silica-gel polygram SILG/UV 254 plates. Melting points were measured by electrothermal IA9100 melting point apparatus in capillary tubes. The starting temperature of the approximate melting range was input via the keyboard, and the melting point range was spotted visually. FT-IR spectra were recorded on a Perkin-Elmer Spectrum BX series, and KBr pellets were used for solid samples. The mass spectrum was obtained using Agilent Technologies 5975C spectrometer via mass selective detector (MSD) operating at an ionization potential of 70 eV^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 400 MHz and 500 MHz in D_2O, DMSO-d_6 and $CDCl_3$ as solvents and (TMS) as the standard for chemical shifts. TGA analysis was performed using TA SDT Q600 V20.9 instrument.

Preparation of the catalyst.

Preparation of 1,4-di(1H-imidazol-1-yl)butane [Bisim]

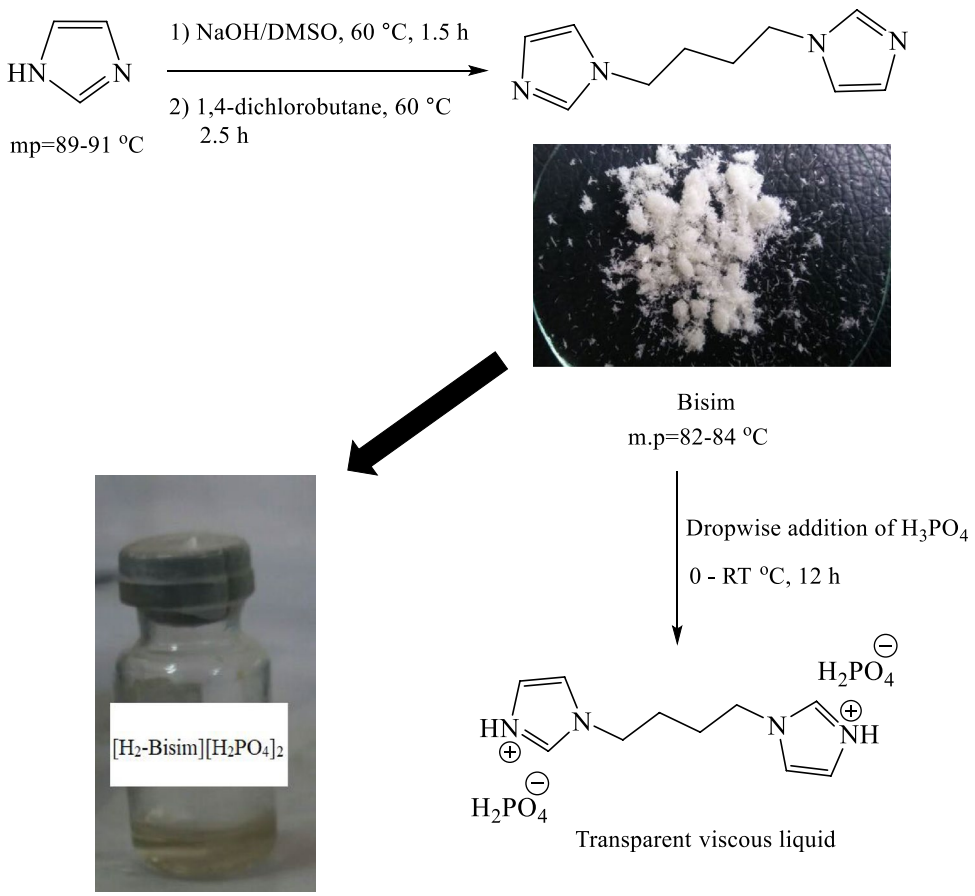
In a 50.0-mL round-bottomed flask, a mixture of imidazole (2.061 g, 30.0 mmol) and sodium hydroxide (1.200 g, 30.0 mmol) in DMSO (10.0 mL) was stirred at 60.0 °C for 1.5 h. Then 1,4-dichloro butane (1.905 g, 15.0 mmol) was added and stirred at similar conditions for 2.5 h. After cooling the mixture, 20 mL of saturated brine solution and crushed ice was added to it with stirring to form white solids. The solid product was filtered and washed with cold water, dried and recrystallized with ethanol. In result, needle-like crystals of 1,4-di(1*H*-imidazol-1-yl)butane (93% yield; M.P. = 82–84 °C) were obtained (Scheme 1).

Spectral data for [Bisim]: FT-IR (KBr, cm^{-1}) $\bar{\upsilon}$.max: 3423, 3124, 2923, 2860, 1543, 1446; ^{1}H NMR (500 MHz, D_2O) δ (ppm): 1.48 (m, 4H, –CH_2–C), 3.38 (t, J = 5.5 Hz, 4H, –CH_2–N), 6.83 (s, 2H, Ar–CH), 6.89 (s, 2H, Ar–CH), 7.42 (s, 2H, N–CH–N); ^{13}C NMR (125 MHz, D_2O) δ (ppm): 26.1, 45.1, 118.9, 126.7, 136.7.

Preparation of 1,1-(butane-1,4-diyl) bis(1H-imidazole-3-ium)dihydrogen phosphate {[H_2-Bisim][H_2PO_4]$_2$}

In a 50.0-mL round-bottomed flask, to 1,4-di(1*H*-imidazole-1-yl)butane (3.802 g, 20.0 mmol) in an ice bath, phosphoric acid 85% (3.0 mL–40 mmol) was added drop-wise and stirred at room temperature for 12 h. The progress of the reaction was monitored using TLC [*n*-Hexane:EtOAc:EtOH (6:5:2)] using an iodine tank before and after separation steps. At the end and after washing the residue with diethyl ether (3 × 20.0 mL) and acetone (2 × 20.0 mL), it was dried using a rotary system under vacuum and it was placed in the oven at 60 °C for 14 h. During this process, a transparent viscous ionic liquid of [H_2-Bisim][H_2PO_4]$_2$ was achieved in 95% yield (Scheme 1). It should be mentioned that the obtained ionic liquid was not soluble in organic solvents. So, D_2O was used as the solvent for NMR spectroscopies (Scheme 1).

Spectral data for [H_2-Bisim][H_2PO_4]$_2$: MS (70 eV, EI): m/z = 386 (M^+); FT-IR (KBr, cm^{-1}) $\bar{\upsilon}$ max: 3420, 2930, 1636, 1274, 1126, 997; ^{1}H NMR (400 MHz, D_2O) (ppm): 1.35 (s, 4H, –CH_2–C), 3.72 (s, 4H, –CH_2–N^+), 6.89 (s, 2H, Ar–H), 6.92 (s, 2H, Ar–H), 8.14 (s, N–CH–N); ^{13}C NMR



Scheme 1. A thumbnail sketch of the preparation of $[H_2\text{-Bisim}][H_2PO_4]_2$

(100 MHz, D_2O) (ppm): 25.71, 48.08, 119.44, 121.17, 133.89. ^{31}P NMR (162 MHz, D_2O) (ppm): −0.53 ($H_2PO_4^-$).

General procedure for the synthesis of arylidene malononitrile and ethyl (*E*)-3-(aryl)-2-cyanoacrylate derivatives

In a 25.0-mL round-bottom flask, a mixture of aromatic aldehyde (1) (1.0 mmol), malononitrile (2) or ethyl cyanoacetate (3) (1.1 mmol) and $[H_2\text{-Bisim}][H_2PO_4]_2$ (0.005 g, 0.013 mmol) in 5.0 mL of $EtOH/H_2O$ (1:1) was stirred magnetically at 80.0 °C for the appropriate time. The reaction process was monitored by TLC [*n*-hexane:ethyl acetate (7:3)]. After cooling of the mixture, 5.0 mL of water was added to it and after the stirring, the solid product was filtered and washed with cold water, dried and recrystallized with ethanol without needing to any extra purification step (Scheme 2).

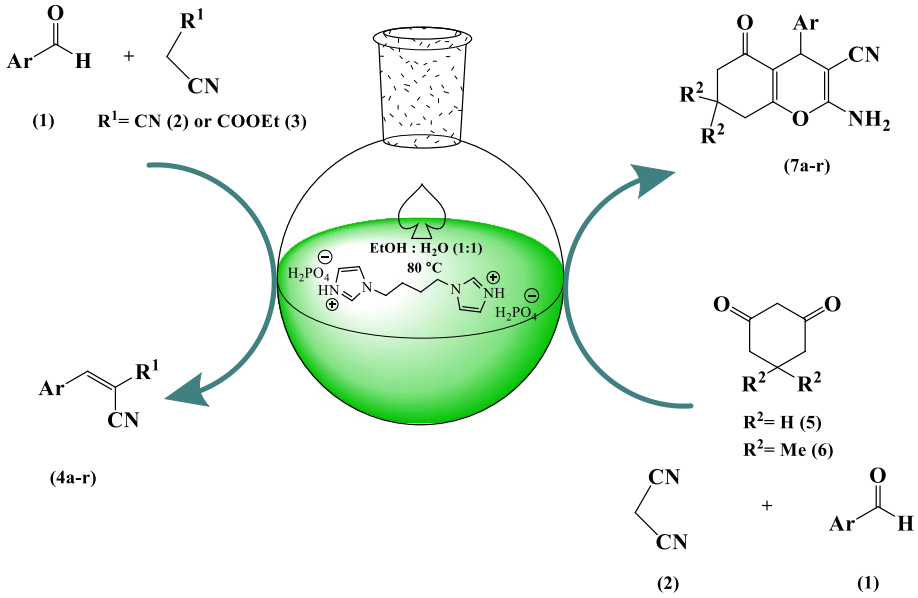
Spectral data of diethyl 3,3′-(1,4-phenylene)(2*E*,2′*E*)-bis(2-cyanoacrylate) [new compound] **(4r)**

White powder (with a very strong fluorescence emission) M.P. = 201–203 °C; FT-IR (KBr, cm^{-1}) $\bar{\upsilon}$ max: 3416, 3030, 2221, 1714,1601, 1456, 1422, 1370, 1307, 1269, 1204, 1138, 1091, 1006, 843, 760, 591, 506; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.42 (t, *J* = 7.0 Hz, 6H), 4.41 (q, *J* = 7.0 Hz, 4H), 8.10 (s. 4H), 8.26 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) *δ* (ppm): 13.12, 62.1, 104.7, 113.9, 130.4, 134.2, 151.7, 160.8.

General procedure for the synthesis of tetrahydrobenzo[*b*]pyran derivatives

In a 25.0-mL round-bottom flask, a mixture of the aromatic aldehyde (1) (1.0 mmol), 1,3-cyclohexanedione (5) or dimedone (6) (1.0 mmol), malononitrile (2) (1.0 mmol) and $[H_2\text{-Bisim}][H_2PO_4]_2$ (0.005 g, 0.013 mmol) in 5.0 mL of $EtOH/H_2O$ (1:1) was stirred magnetically at 80.0 °C for the appropriate time. The progress of the reaction was followed by TLC (*n*-hexane:ethyl acetate; 7:3). After cooling of the mixture, 5.0 mL of water was added to it and after the stirring, the solid product was filtered and washed with cold water, dried and recrystallized with ethanol without needing to any extra purification step (Scheme 2).

Spectral data of 2-amino-4-(4-cyanophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile [new compound] **(7r)**



Scheme 2. The synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran derivatives

White powder; M.P. = 236–238 °C; FT-IR (KBr, cm^{-1}) ῡ max: 3421, 3333, 3254, 3216, 3024, 2964, 2917, 2866, 2271, 2199, 1681, 1650, 1602, 1498, 1413, 1356, 1260, 1206, 1167, 1127, 1088, 1004, 909, 838, 630;^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm):1.86–2.0 (m, 2H), 2.22–2.34 (m, 2H), 2.57–2.67 (m, 2H), 4.30 (s, 1H), 7.16 (s, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 19.2, 25.9, 35.2, 56.5, 108.7, 112.3, 118.3, 118.9, 127.8, 131.8, 149.7, 157.9, 164.6, 195.3.

Results and discussion

In recent years, the introduction of new catalysts for the promotion of organic transformation has become an important part of our ongoing research program [55–64]. In this line of work, we focused a part of our attention on the design, synthesis, characterization and application of Brønsted acidic ionic liquids [57, 59, 64–67]. Herein and in continuation of the studies, we report the preparation of $[H_2\text{-Bisim}][H_2PO_4]_2$ and its characterization by the use of FT-IR, ^{1}H NMR, ^{13}C NMR, ^{31}PNMR and mass spectroscopies. Based on the obtained results, we concluded that this compound can be used as an efficient catalyst for the acceleration of the reactions needing an acidic catalyst to speed-up. So, in continue, the ability of this ionic liquid was studied in the promotion of the synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran derivatives.

Characterization of the catalyst

FT-IR analysis

By the comparison of the FT-IR spectra of imidazole and bis imidazole, we can see a decrease in the number and severity of the peaks in the bis form which can be due to reduction in vibrations caused by the movement of the relatively locked structure range. In the FT-IR spectra of $[H_2\text{-Bisim}][H_2PO_4]_2$, the broadening of the absorption line between 2700 and 3300 cm^{-1} is because of acidic hydrogen bonds. The broad absorption band at 3420 cm^{-1} can be relevant to N–H stretching vibrations. The bands which are located at 2980 cm^{-1} and 2930 cm^{-1} can be assigned to C-H stretching vibrations. Dihydrogen phosphate stretching bands appeared between 800 and 1250 cm^{-1}. The bands at 1126 cm^{-1} and 1074 cm^{-1} are related to P = O while P-O sharp band occurred at 997 cm^{-1} and O=P–O vibrations occurred at 625 cm^{-1} and 497 cm^{-1}.

NMR spectroscopy

In the ^{1}H NMR spectrum of 1,4-di(1*H*-imidazol-1-yl) butane, five peaks related to five types of hydrogens are observed. A multiplet peak at 1.46–1.49 ppm for H_a, a triplet peak at 3.38 ppm for H_b, three single peaks at 6.83 ppm, 6.89 ppm and 7.42 for H_c, H_d and H_e which are related to the imidazole ring.

^{13}C NMR also shows two peaks at 26.1 ppm (related to C_1) and 45.1 ppm (related to C_2) in the aliphatic area related to the alphatic chain and three peaks at 118.9 ppm, 126.7 ppm and 136.7 ppm (related to C_3, C_4 and C_5) that are related to the imidazole moiety.

In the ^{1}H NMR spectra of $[H_2\text{-Bisim}][H_2PO_4]_2$, two singlet peaks are observed in aliphatic area at 1.35 ppm for H_a and 3.72 ppm for H_b. The peaks of two nearby aromatic hydrogens of the imidazole ring (H_c and $H_{d)}$ are appeared as three singlets at 6.89 ppm and 6.92 ppm. In this spectrum, H_e can be observed at 8.14 ppm. The hydrogen of NH^+ due to its acidity is rapidly exchanged with deuteriums of the solvent and is not observable in D_2O.

It should be mentioned that the comparison of the NMR spectrums of [Bisim] and $[H_2\text{-Bisim}][H_2PO_4]_2$ shows a downfield shift in $[H_2\text{-Bisim}][H_2PO_4]_2$ (from 7.42 ppm for Bisim to 8.15 ppm) for He that can be related to the positive charge induced on the nitrogen atom after receiving H^+ from H_3PO_4 (Scheme 3).

In the ^{13}C NMR spectra, the peaks at 25.7 ppm and 48.1 ppm can be related to C_1 and C_2 of CH_2 of the aliphatic chain. Also, the peaks at 119.4 ppm, 121.2 ppm and 133.9 ppm are related to aromatic C_3, C_4 and C_5 of the imidazole ring, respectively.

Since the catalyst is not soluble in organic solvents, when D_2O is used as the solvent, the acidic hydrogens do not appear in the ^{1}H NMR spectrum. So, ^{31}P NMR spectroscopy is utilized to show the existence of dihydrogen phosphate anions in the structure of the catalyst. A singlet peak at −0.53 ppm is attributed to the phosphorus atom of $H_2PO_4^-$ in comparison with the 0.00 ppm for H_3PO_4 (85%) which is the accepted standard reference in the ^{31}P NMR spectroscopy.

Mass spectroscopy

In the mass spectrum of $[H_2\text{-Bisim}][H_2PO_4]_2$, the molecular ion peak (M^+) appeared at m/e = 386 which corresponds to the mass of the catalyst. Other peaks related to other fragments can be observed in this spectrum.

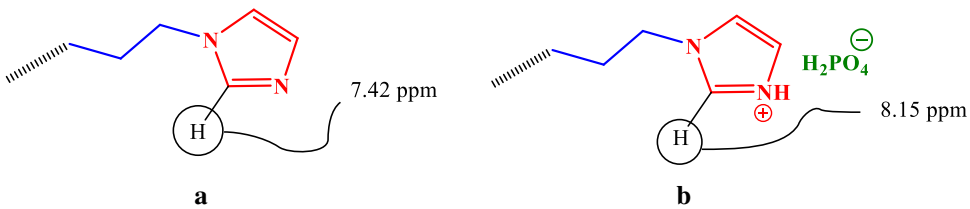
TGA analysis

TGA analysis of the $[H_2\text{-Bim}][H_2PO_4]_2$ shows a little weight loss until about 110 °C which is due to the loss of moisture. From 200 °C, a gently and uniform decrease in weight is observable until 400 °C and then the slope of the diagram shows an increase in weight loss. This trend is normal for an organic-based ionic compound. The result shows that the introduced ionic liquid is completely stable in the optimized temperature of the reactions.

Catalytic activity

To show the catalytic ability of $[H_2\text{-Bisim}][H_2PO_4]_2$ as a new acidic ionic liquid, the synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*] pyran derivatives studied using this catalyst was investigated in various conditions. The effect of the amounts of the catalyst, temperature and solvent in the synthesis of the mentioned compounds was studied, and the obtained results are collected in Tables 1 and 2.

As shown in Tables 1 and 2, in the absence of catalyst the reaction is not completed and only trace amounts of the product are formed. The results show that the use of the catalyst in both reactions are important. Also, the obtained results reveal that the use of the aqueous solvents led to an improvement in the yield of both of the reactions. The best



Scheme 3. The difference of chemical shift (^{1}HNMR in D_2O) of the mentioned hydrogen in [Bisim] (**a**) and $[H_2\text{-Bisim}][H_2PO_4]_2$ (**b**)

Table 1 Optimization of the amount of the catalyst, temperature and solvent in the synthesis of arylidene malononitrile derivative of 4-chlorobenzaldehyde **4b**

Entry	Amount of catalyst (mol %)	Solvent	Temp. (°C)	Time (min)	Conversion (yield) (%)
1	–	–	100	120	Not completed
2	2.6	–	100	120	Not completed
3	2.6	$CHCl_3$	Reflux	120	Trace
4	2.6	C_2H_5OH	Reflux	120	Not completed
5	2.6	CH_3CN	Reflux	120	100 (55)[a]
6	1.3	H_2O	r.t	120	Not completed
7	1.3	H_2O	Reflux	45	100 (90)[a]
8	1.3	C_2H_5OH	Reflux	55	100 (74)
9	1.3	C_2H_5OH:H_2O (1:1)	r.t	120	Not completed
10	2.6	C_2H_5OH:H_2O (1:1)	Reflux	34	100 (83)[a]
11	1.3	C_2H_5OH:H_2O (1:1)	80	15	100 (96)[a]
12	1.3	C_2H_5OH:H_2O (1:1)	Reflux	13	100 (87)[a]
13	1.0	C_2H_5OH:H_2O (1:1)	80	22	100 (89)[a]

[a]Isolated yields

Table 2 Optimization of the amount of the catalyst, temperature and solvent in the synthesis of tetrahydrobenzo[*b*] pyran derivative of 4-chlorobenzaldehyde **7o**

Entry	Amount of catalyst (mol %)	Solvent	Temp. (°C)	Time (min.)	Conversion (yield) (%)
1	–	–	100	120	Not completed
2	2.6	–	100	120	Not completed
3	2.6	CH_3CN	r.t	120	Not completed
4	2.6	CH_3CN	Reflux	120	Not completed
5	2.6	H_2O	Reflux	85	100 (81)[a]
6	1.3	H_2O	Reflux	60	100 (79)[a]
7	1.3	H_2O	80	70	100 (88)[a]
8	1.3	C_2H_5OH	Reflux	85	100 (69)[a]
9	1.3	C_2H_5OH: H_2O (1:1)	r.t	120	Not completed
10	2.6	C_2H_5OH: H_2O (1:1)	Reflux	55	100 (70)[a]
11	1.3	C_2H_5OH: H_2O (1:1)	Reflux	32	100 (86)[a]
12	1.3	C_2H_5OH: H_2O (1:1)	80	35	100 (91)[a]
13	1.0	C_2H_5OH: H_2O (1:1)	80	48	100 (84)[a]

[a]Isolated yields

conditions for both of the reactions were determined in the presence of 1.3 mol% of the catalyst, mixture of water and ethanol [1:1] as solvent at 80 °C (Scheme 2).

In continue, aldehydes containing both electron-withdrawing and electron-donating substituents were used under the optimized conditions in both reactions. The data showed that all the studied reactions were carried out in short times and high yields. Moreover, the nature and electronic properties of the substituents had no obvious effect on the rate and reaction yields (Tables 3 and 4).

Mechanistic study

The proposed mechanisms of the studied reactions are shown in Scheme 4. In the beginning, the carbonyl group of aldehyde (**1**) is activated by hydrogen bonding from the catalyst

Table 3 Preparation of arylidene malononitrile and ethyl (*E*)-3-(aryl)-2-cyanoacrylate derivatives using $[H_2\text{-Bisim}][H_2PO_4]_2$ as the catalyst

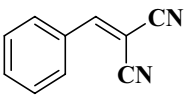
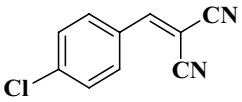
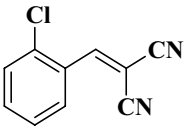
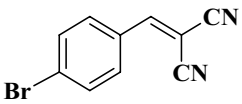
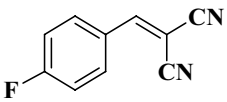
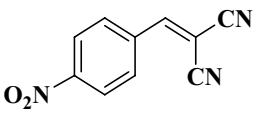
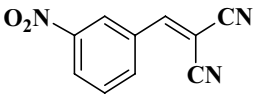
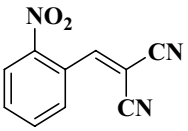
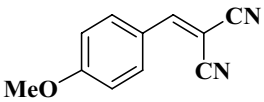
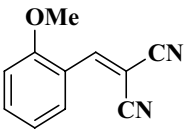
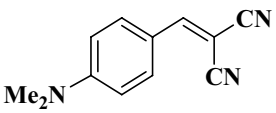
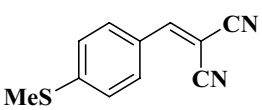
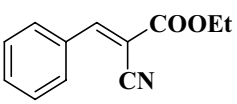
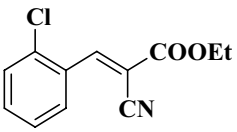
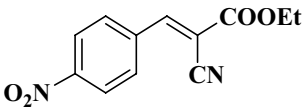
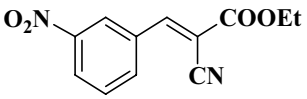
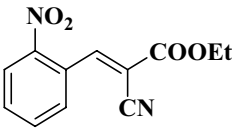
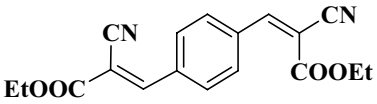
Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M. P. (°C)		Ref
						Found	Rep	
1	C_6H_5CHO		**4a**	22	83	80–83	82	[37]
2	$4\text{-}ClC_6H_4CHO$		**4b**	15	96	161–163	162–164	[36]
3	$2\text{-}ClC_6H_4CHO$		**4c**	11	93	91–94	92–93	[34]
4	$4\text{-}BrC_6H_4CHO$		**4d**	16	92	162–163	158	[26]
5	$4\text{-}FC_6H_4CHO$		**4e**	12	90	124–126	124	[26]
6	$4\text{-}NO_2C_6H_4CHO$		**4f**	17	94	160–162	157–159	[27]
7	$3\text{-}NO_2C_6H_4CHO$		**4g**	15	91	100–102	102–104	[27]
8	$2\text{-}NO_2C_6H_4CHO$		**4h**	5	95	134–138	142	[26]
9	$4\text{-}MeOC_6H_4CHO$		**4i**	36	89	113–114	115–117	[25]
10	$2\text{-}MeOC_6H_4CHO$		**4j**	50	88	82–84	81–82	[34]
11	$4\text{-}Me_2NC_6H_4CHO$		**4k**	38	87	180–182	179	[26]
12	$4\text{-}SMeC_6H_4CHO$		**4l**	19	90	155–157	155–157	[33]
13	C_6H_5CHO		**4m**	26	84	47–49	46–48	[36]

Table 3 (continued)

Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M. P. (°C)		Ref
						Found	Rep	
14	2-ClC_6H_4CHO		**4n**	13	90	57–58	55	[68]
15	4-$NO_2C_6H_4CHO$		**4o**	22	94	159–161	166–168	[36]
16	3-$NO_2C_6H_4CHO$		**4p**	19	90	74–75	76	[69]
17	2-$NO_2C_6H_4CHO$		**4q**	29	93	100–101	98–100	[36]
18	1,4-$C_6H_4(CHO)_2$		**4r**	32	92	201–203	New	–

[a]Isolated yield

to produce the intermediate **a**. Intermediate **a** is attacked by the tautomer form of the compound containing the activated methylene group (**2** or **3**) to produce intermediate **b** and it loses a molecule of water leading to the Knoevenagel condensation product (**4a-r**). In the other way, these products can be attacked by enol form of 1,3-diketone (**5** or **6**) in a Micheal-type reaction to give the intermediate **c**. Finally, cyclocondensation of **c** gives **d** which can be converted to the desired product **(7a–r).**

Reusability of the catalyst

The synthesis of 2-(4-chlorobenzylidene)malononitrile **4b** and 2-amino-4-(4-chlorophenyl)-7,7-dimetyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile **7b** was picked out to survey the reusability of the catalyst. After completion of the reaction, the reaction mixture was filtered off and the recovered catalyst was attained by evaporating the solvent under vacuum conditions. Then, the obtained residue was washed with diethyl ether and reused five times with the least decrease in its performance for both of the reactions (Figs. 1 and 2).

To compare the performance and efficiency of the introduced catalyst with other reported ones in the literature in the synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran derivatives, we appointed the results of the synthesis of 2-(4-chlorobenzylidene) malononitrile **4b** and 2-amino-4-(4-chlorophenyl)-7,7-dimetyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile **7b**. Investigation on the results from the viewpoints of the amounts of the catalyst, reaction times and yields show that $[H_2\text{-Bisim}][H_2PO_4]_2$ had one or more advantages in comparison with other mention catalysts (Tables 5 and 6).

Table 4 Preparation of tetrahydrobenzo[*b*]pyran derivatives using $[H_2\text{-Bisim}][H_2PO_4]_2$ as the catalyst

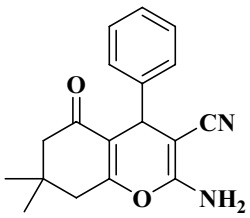
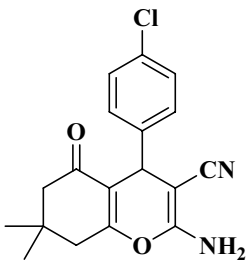
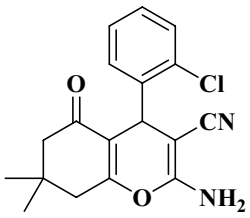
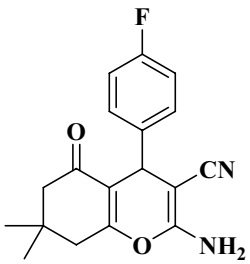
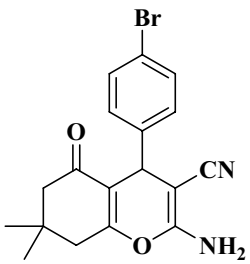
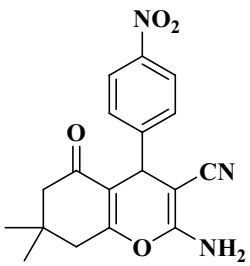
Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M. P. (°C)		Ref
						Found	Rep	
1	C_6H_5CHO		**7a**	60	95	230–232	225–227	[37]
2	$4\text{-}ClC_6H_4CHO$		**7b**	35	91	206–207	208–210	[34]
3	$2\text{-}ClC_6H_4CHO$		**7c**	20	89	212–214	216–218	[37]
4	$4\text{-}FC_6H_4CHO$		**7d**	25	86	170–173	171–174	[39]
5	$4\text{-}BrC_6H_4CHO$		**7e**	34	87	202–204	199–201	[39]
6	$4\text{-}NO_2C_6H_4CHO$		**7f**	10	93	178–180	176–179	[39]

Table 4 (continued)

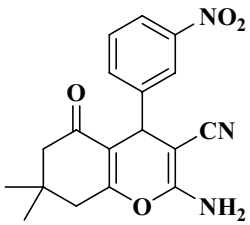
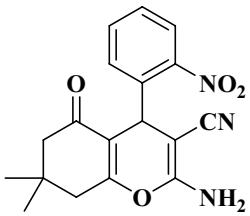
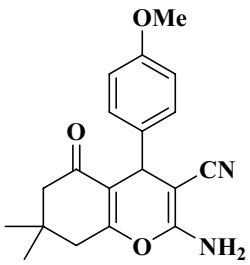
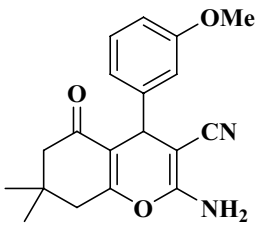
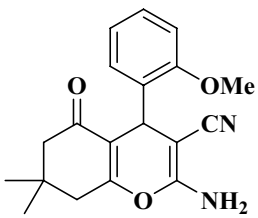
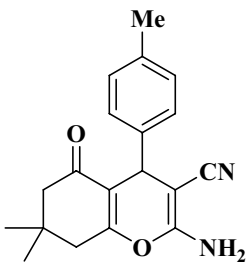
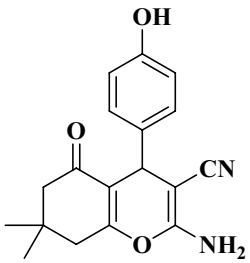
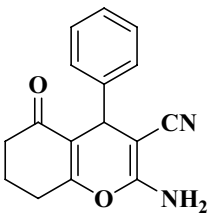
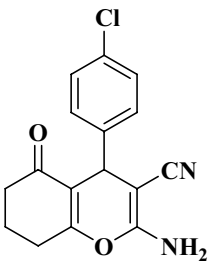
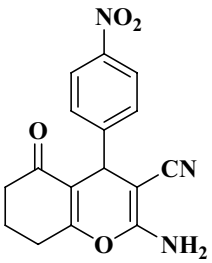
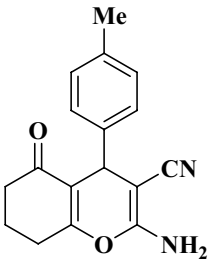
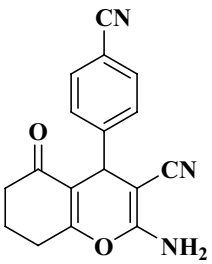
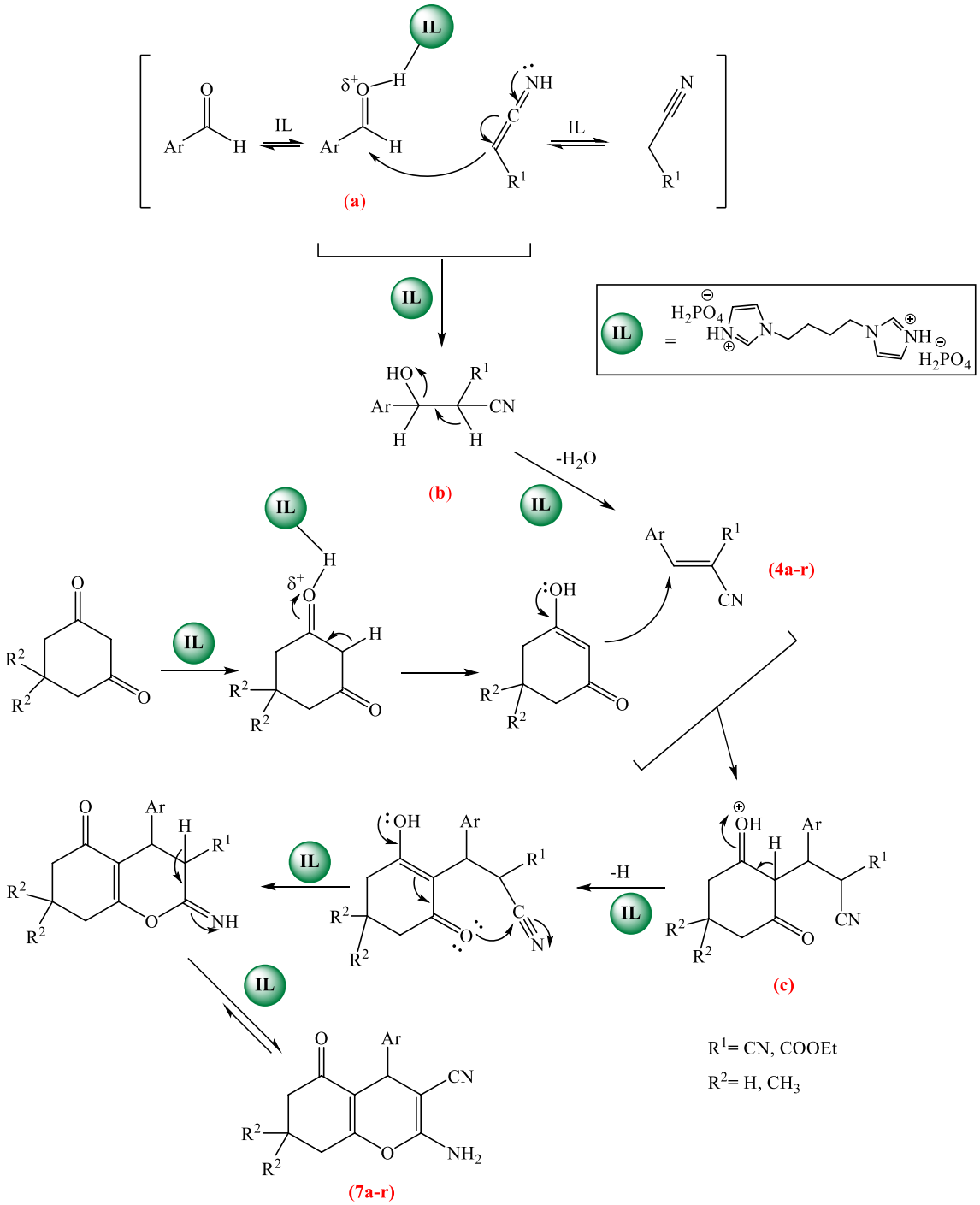
Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M. P. (°C)		Ref
						Found	Rep	
7	3-$NO_2C_6H_4CHO$		**7g**	16	85	210–212	214–215	[39]
8	2-$NO_2C_6H_4CHO$		**7h**	6	90	210–212	213–217	[39]
9	4-$OMeC_6H_4CHO$		**7i**	49	88	196–198	195–196	[37]
10	3-$OMeC_6H_4CHO$		**7j**	31	91	202–204	208–210	[49]
11	2-$OMeC_6H_4CHO$		**7k**	49	89	200–202	202–204	[37]
12	4-MeC_6H_4CHO		**7l**	73	89	212–214	217–219	[34]

Table 4 (continued)

Entry	Aldehyde	Product		Time (min)	Yield (%)[a]	M. P. (°C)		Ref
						Found	Rep	
13	4-OHC_6H_4CHO		**7m**	50	90	209–211	210–214	[39]
14	C_6H_5CHO		**7n**	52	95	210–212	212–214	[34]
15	4-ClC_6H_4CHO		**7o**	45	91	222–224	224–226	[47]
16	4-$NO_2C_6H_4CHO$		**7p**	12	94	235–236	230–232	[47]
17	4-MeC_6H_4CHO		**7q**	75	88	220–223	224–226	[54]
18	4-CNC_6H_4CHO		**7r**	46	93	236–238	New	-

[a]Isolated yield



Scheme 4. Pastulated mechanism for the synthesis of the requested target molecules

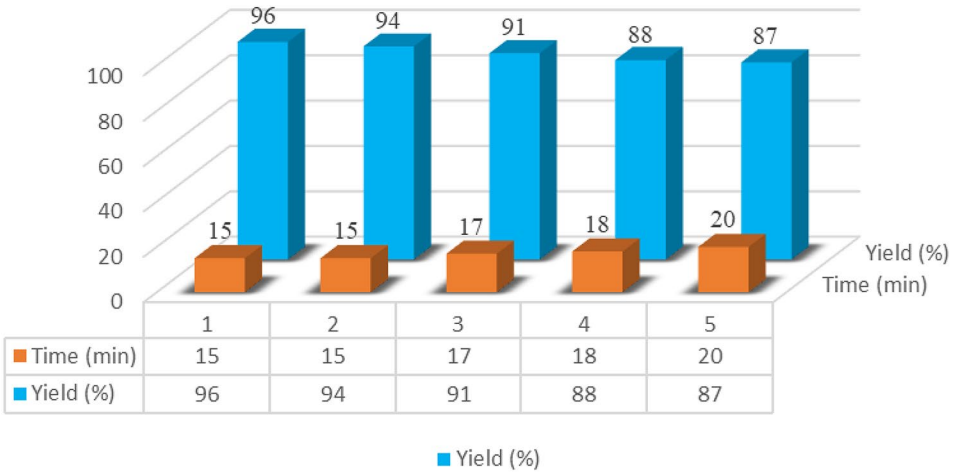


Fig. 1 Reusability of $[H_2\text{-Bisim}][H_2PO_4]_2$ in the synthesis of 2-(4-chlorobenzylidene)malononitrile **4b**

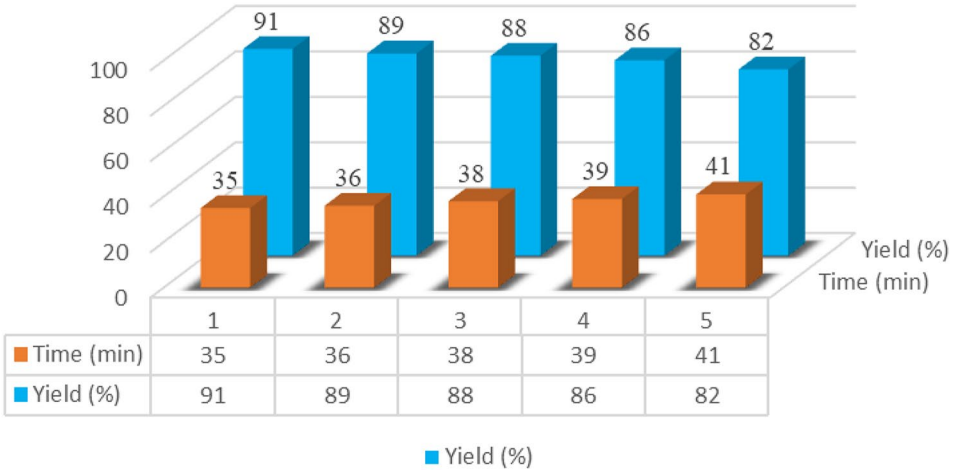


Fig. 2 Reusability of $[H_2\text{-Bisim}][H_2PO_4]_2$ in the synthesis of 2-amino-4-(4-chlorophenyl)-7,7-dimetyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile **7b**

Table 5 Comparison of the activity of $[H_2\text{-Bisim}][H_2PO_4]_2$ with other reported catalysts in the synthesis of 2-(4-chlorobenzylidene) malononitrile **4b**

Entry	Catalyst	Amount (mol)	Conditions	Time (min)	Yield (%)	TOF (s^{-1})	Ref
1	Cetyltrimethyl ammonium bromide (CTMAB)	2×10^{-4}	H_2O/r.t	90	95.5	88.42	[23]
2	Lemon juice	1 mL	Solvent-free/r.t	60	87	–	[26]
3	Silica-*L*-proline	1×10^{-4}	CH_3CN/80 °C	540	95	29.32	[27]
4	MgO/ZrO_2	2×10^{-4}	Solvent-free/60 °C	20	65	270.83	[28]
5	Graphene oxide (GO)	0.5 mL	Solvent-free/r.t	180	96	–	[32]
6	Mesoporous titanosilicate Ti-TUD-1	1×10^{-4}	C_2H_5OH/r.t	40	84	350	[33]
7	Na_2S/Al_2O_3	2×10^{-4}	CH_2Cl_2/r.t	30	90	250	[68]
8	$[H_2\text{-Bisim}][H_2PO_4]_2$	0.26×10^{-4}	H_2O: C_2H_5OH (1:1)/80 °C	15	96	4102.56	This work

Table 6 Comparison of the activity of $[H_2\text{-Bisim}][H_2PO_4]_2$ with other reported catalysts in the synthesis of 2-amino-4-(4-chlorophenyl)-7,7-dimetyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile **7b**

Entry	Catalyst	Amount (mol)	Conditions	Time (min.)	Yield (%)	TOF (s^{-1})	Ref
1	*p*-Dodecylbenzenesulfonic acid	4×10^{-4}	H_2O/Reflux	240–420	69	–	[44]
2	2,2,2-Trifluoroethanol (TFE)	2 mL	Reflux	300	95	–	[45]
3	Phenylboronic acid	0.5×10^{-4}	H_2O:C_2H_5OH (1:1)/Reflux	30	84	933.33	[46]
4	1,4-Diazabicyclo[2.2.2]octane (DABCO)	1×10^{-4}	H_2O/Reflux	120	94	130.56	[48]
5	H_2PO_4-SCMNPs	0.03 g	Solvent-free/60 °C	25	89	–	[49]
6	Hexadecyldimethylbenzyl ammonium bromide (HDMBAB)	1.2×10^{-4}	H_2O/80–90 °C	450	90	27.78	[50]
7	*N,N,N*-Triethyl-N-butanesulfonic acid ammonium hydrogen sulfate ([TEBSA]HSO_4)	5×10^{-4}	H_2O/90 °C	60	91	50.56	[51]
8	*L*-Pyrrolidine-2-carboxylic acid sulfate (LPCAS)	1×10^{-3}	H_2O/Reflux	15	85	94.44	[52]
9	Na_2SeO_4	0.1 g	H_2O:C_2H_5OH (1:1)/ Reflux	180	90	–-	[53]
10	$[H_2\text{-Bisim}][H_2PO_4]_2$	0.13×10^{-4}	H_2O:C_2H_5OH (1:1)/80 °C	35	91	3333.33	This work

Conclusions

In this study, 1,1-(butane-1,4-diyl)bis(1*H*-imidazole-3-ium)dihydrogen phosphate is simply prepared and characterized by a variety of techniques. This new ionic liquid can be used as a catalyst to accelerate the preparation of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran derivatives. This method shows some distinct advantages such as short reaction times, high yields, use of non-expensive materials, mild reaction conditions, easy and straightforward procedure for work-up, not using hazardous organic solvents and use of a reusable catalyst. Preparation of this catalyst using imidazole which is not a toxic compound and phosphoric acid (which even uses in some drinks) makes this new acidic ionic liquid a distinguished selection regarding the environmental issue and green chemistry concepts. Another brilliant property of this new ionic liquid is its high stability. Based on over-observation, this catalyst can be stored in a refrigerator and can be used several times during six months without loss of its catalytic ability and changes in its physical appearance and properties, what that usually most of the ionic especially acidic ones do not have.

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

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