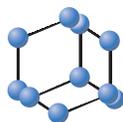
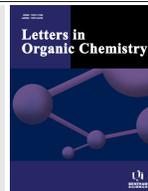


RESEARCH ARTICLE

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SCIENCE[Bmim][CF₃COO] as a Solvent and a Catalyst for the Knoevenagel CondensationNguyen Thi Chung¹, Vo Cong Dung² and Dau Xuan Duc^{1,*}¹Department Chemistry, School of Education, Vinh University, Vinh City, Vietnam; ²Center for Education Accreditation, Vinh University, Vinh City, Vietnam

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Abstract: A facile and green strategy for the Knoevenagel condensation reaction of aryl aldehydes and active methylene compounds using [Bmim][CF₃COO] ionic liquid as a solvent and a catalyst has been introduced. The method features some advantages such as good to excellent yield of products, relatively short reaction time, mild reaction conditions, broad substrate scope, and scalability. Moreover, the ionic liquid solvent could be conveniently recycled and reused up to three times without any considerable loss of catalytic activity. Twelve products were obtained in high yields, and their structures were confirmed by NMR data. A plausible reaction mechanism involving the role of the ionic liquid catalyst was also suggested.

Keywords: Ionic liquid, methylene compounds, ethyl cyanoacetate, malonitrile, diethyl malonate, benzaldehyde.

1. INTRODUCTION

The Knoevenagel condensation reaction is one of the most straightforward and versatile methods for the synthesis of α,β -unsaturated compounds [1] as well as coumarines [2] from active methylene compounds and aldehydes or ketones. α,β -Unsaturated compounds, especially benzylidenemalonitrile derivatives, play important roles in the synthesis of many fine chemicals, such as dyes, herbicides, fragrances, and optoelectronic materials [3-6]. Several benzylidenemalonitrile derivatives have been found to possess valuable bioactivities, such as 2-(4-nitrobenzylidene) malonitrile and 2-(3,4,5 trimethoxybenzylidene) malonitrile as potent tyrosine kinase inhibitors [7, 8] and 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile (Fig. 1) [9, 10] as antibacterial against *B. cereus*, *S. aureus*, and *S.*

Unsurprisingly, the Knoevenagel condensation has drawn great research attention, and numerous synthetic strategies have been reported. Originally, the Knoevenagel reaction was performed using base catalysts like primary or secondary amines [11, 12]. A wide range of Lewis acids, such as TiCl₄, ZnCl₂, CeCl₃·7H₂O, NbCl₅, Mg(ClO₄)₂, and SmI₃, has been successfully employed as catalysts for this condensation reaction [13-18]. The use of easily recyclable nano-material catalysts for the Knoevenagel condensation reaction has been widely utilized [19-21]. Metal-organic framework, an innovative material, has also been employed as catalysts for this reaction [22-24]. Moreover, the use of microwave irradiation as an energy source for this transformation has been well-documented [25, 26].

Recently, the employment of ionic liquids as catalysts and green solvents for organic reactions, which could improve reaction yield as well as decrease reaction time, has attracted the intensive interest of chemists [27-29]. A diverse range of ionic liquids have been employed for this reaction, such as [C6-mim]PF₆, [bmim]Cl·xAlCl₃ and [bpy]Cl·xAlCl₃, [Bmim]BF₄, guanidinium lactate ionic liquid, ethylammonium nitrate (EAN), and [bmim]OH [30-36].

Driven by the unique properties of ionic liquids, we report herein the Knoevenagel condensation between aryl aldehydes and ethyl cyanoacetate or malonitrile or diethyl malonate using [Bmim]TFA as a green solvent as well as a highly efficient catalyst. Mild reaction conditions, short reaction time, high yields of products, and recyclability of catalyst are the main attractive features of the synthesis.

2. RESULTS AND DISCUSSION

In search for the best experimental condition, *p*-methoxy benzaldehyde **1a** and ethyl cyanoacetate **2a** were chosen as model substrates for the Knoevenagel condensation reaction. A mixture of ethyl cyanoacetate (2 mmol) and *p*-methoxy benzaldehyde (2.2 mmol) in different ionic liquids (5 mL) was stirred for stated time at room temperature to evaluate their efficiency for promoting the Knoevenagel reaction. The progress of the reaction was monitored by thin-layer chromatography. The results are mentioned in Table 1.

As mentioned in the table, all ionic liquids showed catalytic activity for the reaction, but different yields of **3a** were obtained. The use of [Bmim]BF₄ gave the desired product **3a** in 83% yields in 1 hour (Table 1, entry1). [Bmim]PF₆, [Bmim][HSO₄], and [Bmim]OAc were much less active. Although a longer time was needed (12 h), reaction yields were decreased to 60%, 48%, and 56%, respectively (Table

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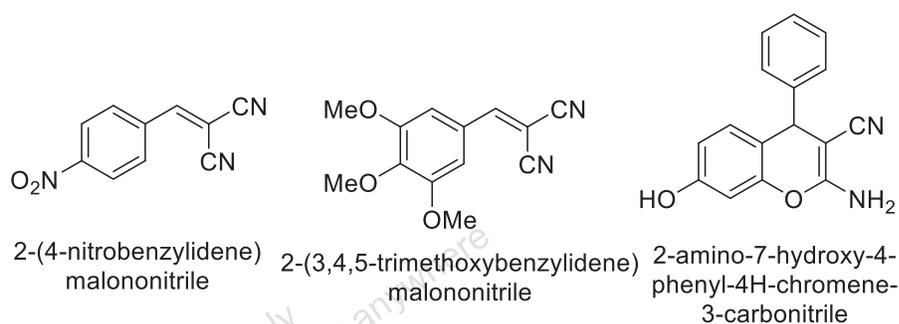
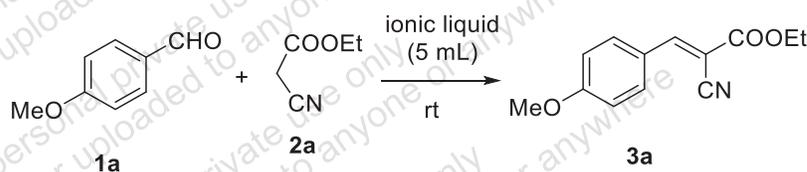


Fig. (1). Several bioactive benzylidenemalononitrile derivatives *epidermidis* [9, 10].

Table 1. Knoevenagel condensation in different ionic liquids.



Entries	Ionic Liquids	Reaction Time	Reaction Yields (%) ^a
1	[Bmim]BF ₄	1 h	83
2	[Bmim]PF ₆	12 h	60, 64 ^b
3	[Bmim][H ₂ SO ₄]	12 h	48, 51 ^b
4	[Bmim]OAc	12 h	56, 59 ^b
5	[Bmim][CF ₃ COO]	1 h	97, (95, 94, 92, 90) ^c
6	[Bmim]OH	2 h	96
7	[Bbim]BF ₄	12 h	78
8	[Bbim]ClO ₄	12 h	65
9	[Bbim]OTf	12 h	68
10	[Bbim]Br	12 h	72
11	[Bnmim]Cl	2 h	91

Note: ^aIsolated yields.

^bThe reaction was performed at 50°C.

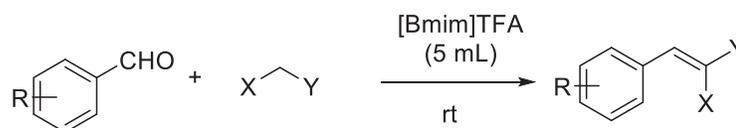
^cThe yields were for 2nd, 3rd, and 4th when [Bmim][CF₃COO] was recycled.

1, entries 2-4). The yields were slightly improved when the reaction was performed at 50°C using these ionic liquids (Table 1, entries 2-4 b). To our delight, an excellent yield of 3a was provided when [Bmim][CF₃COO] was employed (Table 1, entry 5). Noticeably, this ionic liquid could be recycled for four additional times without any considerable decrease in reaction yields. Product was achieved in 90-95% yields for the three next runs of recycled ionic liquid. Two other ionic liquids, [Bmim]OH and [Bmmim]Cl, also delivered 3a in excellent yields, although a longer reaction time was required (Table 1, entries 6 and 11). The employment of [Bbim]BF₄, [Bbim]ClO₄, [Bbim]OTf, and [Bbim]Br afforded product in moderate yields (78, 65, 68, and 72%, respectively) in 12 h (Table 1, entries 7-1). Considering the reaction time and yield of the product, [Bmim][CF₃COO] was

chosen as the optimum catalyst to perform the Knoevenagel condensation at room temperature.

With the optimum conditions in hand, the generality and scope of the developed protocol were expanded for a variety of aryl aldehydes and methylene compounds, including ethyl cyanoacetate, malonitrile, and diethyl malonate. The results are listed in Table 2.

As illustrated in Table 2, various aromatic aldehydes with electron-donating groups (methoxyl and dimethyl amino) and electron-withdrawing groups (fluoro, nitro, and cyano) reacted easily with three active methylene compounds under optimum conditions to furnish products in good to excellent yields. There was no obvious electronic effect of substituents on the aromatic ring of aldehydes to reaction yield. Ethyl cyanoacetate reacted with *p*-methoxy benzaldehyde,

Table 2. The Knoevenagel condensation of aryl aldehydes with methylene compounds in [Bmim][CF₃COO].

Entries	X	Y	R	Products	Yields (%)
1	CN	COOEt	4-OMe	3a	97 (93 ^a)
2	CN	COOEt	2-OMe	3b	83
3	CN	COOEt	4-F	3c	96
4	CN	COOEt	4-CN	3d	95
5	CN	COOEt	4-NO ₂	3e	98
6	CN	CN	4-OMe	3f	96
7	CN	CN	4-F	3g	94
8	CN	CN	4-NO ₂	3h	97
9	COOEt	COOEt	H	3i	93
10	COOEt	COOEt	4-F	3j	94
11	COOEt	COOEt	4-OMe	3k	92
12	COOEt	COOEt	4-(CH ₃) ₂ N	3l	91

Note: ^aIsolated yields.

^bThe reaction was performed with 10 mmol of ethyl cyanoacetate.

Table 3. Yields of **3a** at different works.

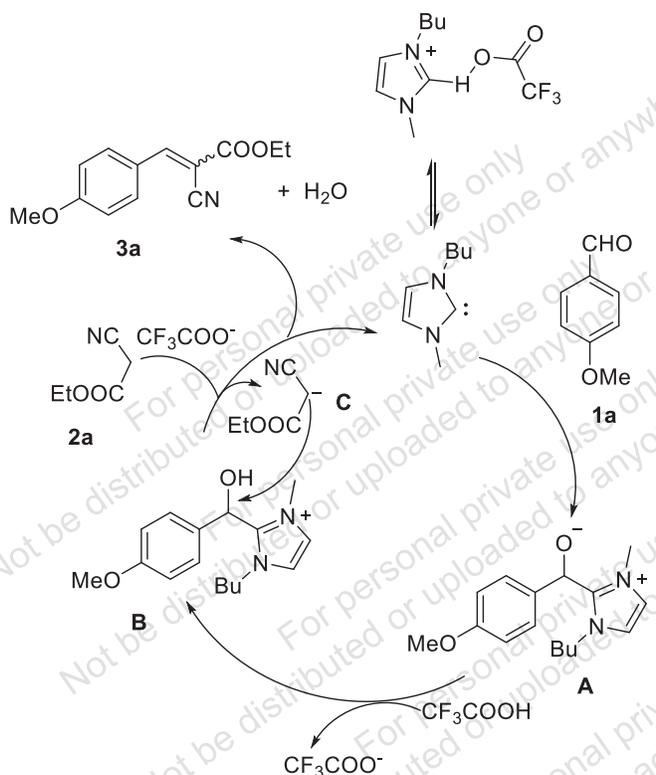
Entries	Catalyst	Time	Solvent	Temperature	Yields (%)
1 ³⁷	Cobalt hydroxyapatite	2 minutes	None	80°C	91%
2 ³⁸	Melamine	50 mins	None	rt	85%
3 ³⁹	Ethylenediammonium diacetate	10 mins	None	rt	92%
4	This work [Bmim] [CF ₃ COO]	1 h	Recyclable [Bmim] [CF ₃ COO]	rt	97%

p-fluorobenzaldehyde, *p*-cyanobenzaldehyde, and *p*-nitrobenzaldehyde to give products in excellent yields (Table 2, entries 1, 3, 4, and 5). The reaction of ethyl cyanoacetate might produce only *E* isomer. The NOESY spectrum of **3a** shows the correlation between the proton of CH₂ of the ethyl group and CH= (the correlation between the proton of CH₂ of the ethyl group and the proton at the ortho position benzene ring was not observed). The reaction between *o*-methoxy benzaldehyde with ethyl cyanoacetate resulted in products in lower yield (83%, Table 2, entry 2), presumably due to the steric effect of the methoxy group at 2-position of aldehyde. Similarly, reactions of malonitrile and diethyl acetate with various benzaldehyde derivatives furnished corresponding products in excellent yield. Another advantage of the protocol is that the synthesis could be applied on a gram scale. In 10 mmol-scale, product **3a** was delivered in 93% yield (Table 2, entry 1a).

To prove the efficiency of the method, we compared the yield of **3a** of our work with previous studies, and the results are illustrated in Table 3. The use of a cobalt hydroxyapatite catalyst led to the rapid formation of the product at higher temperatures, although the yield was lower (Table 3, entry 1) [37]. Under melamine catalysis, only a moderate yield of **3a** was observed (Table 3, entry 2) [38]. The ionic liquid ethylenediammonium diacetate was also found to be an efficient catalyst for the Knoevenagel condensation (Table 3, entry 3,4), but again, using this, the reaction yield was observed to be slightly lower [39].

The tentative reaction mechanism for the reaction between **1a** and **2a** is illustrated in Scheme 1. In this specific case, the formation of the final product would be mediated by the 1-butyl-3-methyl-imidazolylene generated from [Bmim][CF₃COO]. This *N*-heterocyclic carbenes (NHC)

might act as a nucleophile attacking the carbonyl group of **1a**, forming a zwitterionic adduct **A**, which was then protonated to give the intermediate **B**. Adding carbanion **C** generating from **2a** to **B** provided **3a** after dehydration. The actual NHC catalyst was also regenerated in this final step.



Scheme 1. Proposed reaction mechanism.

3. METHODS AND EXPERIMENT

3.1. Materials

All chemicals and ionic liquid were purchased from Sigma-Aldrich and used directly without any further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker NMR Spectrometer instrument (running at 500 MHz and 125 MHz, respectively). CDCl_3 was used as a solvent, and TMS was used as an internal standard. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) are expressed in hertz (Hz).

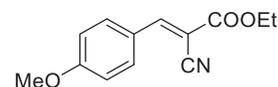
3.2. General Procedure for the Knoevenagel Condensation Reaction

4-Methoxy benzaldehyde (**1a**, 226 mg, 2 mmol) and ethyl cyanoacetate (**2a**, 299 mg, 2.2 mmol, 1.1 equiv) were added to a flask containing 5 mL of $[\text{Bmim}][\text{CF}_3\text{COO}]$ equipped with a magnetic stirring bar. The mixture was allowed to stir for 1 h at room temperature. The course of the reaction was monitored by TLC. After the reaction was completed, the mixture was extracted with diethyl ether (3x10 mL). The organic extracts were combined, and the solvent was evaporated. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as eluent (98:2) to provide the corresponding product **3a** as a white solid (448 mg, 97% yield). The ionic liquid

was kept under a high vacuum (4 mm Hg) at 60°C for 3 h to remove volatiles. The ionic liquid could then be used directly for the next run.

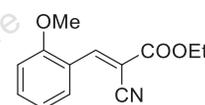
3.3. Experimental Details

3.3.1. Ethyl (E)-2-cyano-3-(4-methoxyphenyl)acrylate (**3a**)



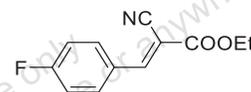
Yellowish solid (448 mg, 97%) ^1H NMR (500 MHz, CDCl_3) δ 8.17 (s, 1H), 8.00 ($J = 8.5$ Hz, 2H), 7.00 ($J = 8.5$ Hz, 2H), 4.37 (q, $J = 7.0$ Hz, 2H), 3.89 (s, 3H), 1.39 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.8, 162.8, 154.3, 133.6, 124.1, 116.1, 114.8, 99.2, 62.2, 55.5, 13.8. NMR data are consistent with the literature report [40].

3.3.2. Ethyl (E)-2-cyano-3-(2-methoxyphenyl)acrylate (**3b**)



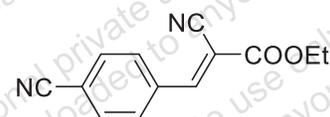
Light yellow solid (383 mg, 83%) ^1H NMR (500 MHz, CDCl_3) δ 8.75 (s, 1H), 8.29-8.27 (m, 1H), 7.53-7.50 (m, 1H), 7.07-7.04 (m, 1H), 4.38 (q, $J = 7.0$ Hz, 2H), 3.90 (s, 3H), 1.40 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.9, 159.5, 150.0, 134.9, 129.3, 121.0, 120.7, 115.8, 111.2, 102.2, 62.5, 55.8, 14.2. NMR data are consistent with the literature report [41].

3.3.3. Ethyl (E)-2-cyano-3-(4-fluorophenyl)acrylate (**3c**)



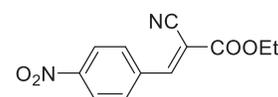
White solid (420 mg, 96%) ^1H NMR (500 MHz, CDCl_3) δ 8.21 (s, 1H), 8.05-8.02 (m, 2H), 7.27-7.18 (m, 2H), 4.39 (q, $J = 7.0$ Hz, 2H), 1.41 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.5 (d, $J = 256.0$ Hz), 162.5, 153.7, 133.6, 128.1, 117.0, 115.1, 102.5, 62.5, 14.2. NMR data are consistent with the literature report [40].

3.3.4. Ethyl (E)-2-cyano-3-(4-cyanophenyl)acrylate (**3d**)



White solid (429 mg, 95%) ^1H NMR (500 MHz, CDCl_3) δ 8.25 (s, 1H), 8.07 (d, $J = 8.5$ Hz, 2H, ArH), 7.80 (d, $J = 8.5$ Hz, 2H, ArH), 4.42 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 161.4, 152.4, 135.2, 133.0, 131.2, 117.7, 116.1, 114.5, 106.8, 63.1, 13.9. NMR data are consistent with the literature report [42].

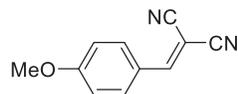
3.3.5. Ethyl (E)-2-cyano-3-(4-nitrophenyl)acrylate (**3e**)



Yellow solid (482 mg, 98%) ^1H NMR (500 MHz, CDCl_3) δ 8.35 ($J = 8.5$ Hz, 2H), δ 8.30 (s, 1H), 8.14 ($J = 8.5$ Hz, 2H),

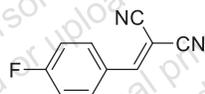
4.42 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.0$ Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.7, 151.5, 150.2, 136.7, 131.6, 124.1, 114.2, 107.4, 63.1, 14.1. NMR data are consistent with the literature report [43].

3.3.6. 2-(4-Methoxybenzylidene)malononitrile (3f)



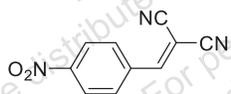
Yellow solid (353 mg, 96%) ¹H NMR (500 MHz, CDCl₃): δ 7.92 ($J = 9.0$ Hz, 2H), 7.68 (s, 1H), 7.03 ($J = 9.0$ Hz, 2H), 3.93 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 164.9, 159.00, 133.6, 124.1, 115.2, 114.5, 113.5, S7 78.4, 55.9. NMR data are consistent with the literature report [40].

3.3.7. 2-(4-Fluorobenzylidene)malononitrile (3g)



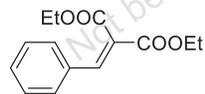
White solid (323 mg, 94%) ¹H NMR (500 MHz, CDCl₃): δ 7.98-7.95 (m, 2H), 7.74 (s, 1H), 7.26-7.22 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 166.2 (d, $J = 259.0$ Hz), 158.5, 133.7, 128.0, 117.2, 113.8, 112.7, 82.51. NMR data are consistent with the literature report [40].

3.3.8. 2-(4-Nitrobenzylidene)malononitrile (3h)



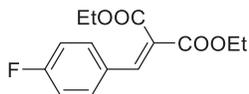
Deep yellow solid (386 mg, 97%) ¹H NMR (500 MHz, CDCl₃): δ 8.38 (d, $J = 9.0$ Hz, 2H), 8.08 (d, $J = 8.8$ Hz, 2H), 7.89 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 157.4, 150.3, 136.0, 131.4, 124.6, 112.8, 111.8, 87.3. NMR data are consistent with the literature report [40].

3.3.9. Diethyl 2-benzylidenemalonate (3i)



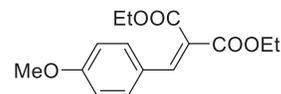
Colorless oil (461 mg, 93%) ¹H NMR (500 MHz, CDCl₃) δ 7.76 (s, 1H), 7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 4.34 (q, $J = 7$ Hz, 2H), 4.24 (q, $J = 7$ Hz, 2H), 1.36 (t, $J = 7.0$ Hz, 3H), 1.31 (t, $J = 7.0$ Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 166.7, 164.1, 142.1, 132.9, 130.5, 129.4, 128.8, 126.1, 61.9, 61.7, 14.15, 14.2, 13.9. NMR data are consistent with the literature report [43].

3.3.10. Diethyl 2-(4-fluorobenzylidene)malonate (3j)



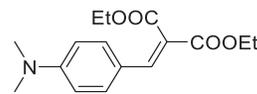
Colorless oil (500 mg, 94%) ¹H NMR (500 MHz, CDCl₃) δ 7.70 (s, 1H), 7.47 (dd, $J = 8.5, 5.5$ Hz, 2H), 7.08 (t, $J = 8.5$ Hz, 2H), 4.38-4.29 (m, 4H), 1.37-1.29 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 166.5 (d, $J = 259.0$ Hz), 164.9, 162.86, 140.8, 131.6, 129.1, 126.1, 116.1, 61.7, 61.5, 14.1, 13.9. NMR data are consistent with the literature report [43].

3.3.11. Diethyl 2-(4-methoxybenzylidene)malonate (3k)



Colorless oil (512 mg, 92%) ¹H NMR (500 MHz, CDCl₃) δ 7.66 ppm (s, 1H), 7.40 ppm (t, $J = 7.5$ Hz, 2H), 6.87 ppm (t, $J = 7.5$ Hz, 2H), 4.34 ppm (q, $J = 7$ Hz, 2H), 4.28 ppm (q, $J = 7$ Hz, 2H), 3.81 ppm (s, 3H), 1.33-1.24 ppm (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 167.4, 164.7, 161.8, 141.8, 131.6, 125.6, 123.9, 114.5, 61.8, 61.6, 55.7, 14.5, 14.1. NMR data are consistent with the literature report [44].

3.3.12. Diethyl 2-(4-(dimethylamino)benzylidene)malonate (3l)



Yellow plates (530 mg, 91%) ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, $J = 8.5$ Hz, 1H), 6.61 (d, $J = 8.5$ Hz, 1H), 4.35 (q, $J = 7.0$ Hz, 1H), 4.25 (q, $J = 7.0$ Hz, 1H), 3.00 (s, 3H), 1.39 – 1.23 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.1, 165.3, 152.1, 142.9, 132.1, 120.4, 120.2, 111.8, 61.6, 61.3, 40.2, 14.4, 14.2. NMR data are consistent with the literature report [44] (Supplementary material).

CONCLUSION

In conclusion, we have developed an efficient and green approach for the Knoevenagel condensation between aryl aldehydes and active methylene compounds using [Bmim][CF₃COO] as a catalyst and a solvent. Relatively short reaction time, mild conditions, scalability, broad substrate scope, and high yield of products are the merits of the proposed method. Furthermore, the ionic catalyst could be reused for three additional runs without a significant decrease in reaction yields. The reaction of aliphatic and heterocyclic aromatic aldehydes, as well as ketones, will be examined and reported in due course.

LIST OF ABBREVIATIONS

Ac	=	Acetyl
Bbim	=	1,3-Di-n-butylimidazolium
Bmim	=	1-Butyl-3-methylimidazolium
Bnmim	=	1-Benzyl-3-Methyl Imidazolium
bpy	=	2,2'-Bipyridine
Bu	=	Butyl
Et	=	Ethyl
Me	=	Methyl
mim	=	Methylimidazolium
TFA	=	Trifluoro acetic

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data and supportive information are available within the article.

FUNDING

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

Declared none.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's website along with the published article.

REFERENCES

- van Beurden, K.; de Koning, S.; Molendijk, D.; van Schijndel, J. *Green Chem. Lett. Rev.*, **2020**, *13*(4), 349-364. <http://dx.doi.org/10.1080/17518253.2020.1851398>
- Vekariya, R.H.; Patel, H.D. *Synth. Commun.*, **2014**, *44*(19), 2756-2788. <http://dx.doi.org/10.1080/00397911.2014.926374>
- Tietze, L.F. *Chem. Rev.*, **1996**, *96*(1), 115-136. <http://dx.doi.org/10.1021/cr950027e> PMID: 11848746
- Fringuelli, F.; Pani, G.; Piermatti, O.; Pizzo, F. *Tetrahedron*, **1994**, *50*(39), 11499-11508. [http://dx.doi.org/10.1016/S0040-4020\(01\)89287-5](http://dx.doi.org/10.1016/S0040-4020(01)89287-5)
- Gómez, R.; Segura, J.L.; Martín, N. *Chem. Commun. (Camb.)*, **1999**, (7), 619-620. <http://dx.doi.org/10.1039/a809405e>
- Segura, J.L.; Martín, N.; Hanack, M. *Eur. J. Org. Chem.*, **1999**, *1999*(3), 643-651. [http://dx.doi.org/10.1002/\(SICI\)1099-0690\(199903\)1999:3<643::AID-EJOC643>3.0.CO;2-V](http://dx.doi.org/10.1002/(SICI)1099-0690(199903)1999:3<643::AID-EJOC643>3.0.CO;2-V)
- Turpaev, K.; Ermolenko, M.; Cresteil, T.; Drapier, J.C. *Biochem. Pharmacol.*, **2011**, *82*(5), 535-547. <http://dx.doi.org/10.1016/j.bcp.2011.05.028> PMID: 21669191
- Turpaev, K.; Drapier, J.C. *Eur. J. Pharmacol.*, **2009**, *606*(1-3), 1-8. <http://dx.doi.org/10.1016/j.ejphar.2009.01.015> PMID: 19374863
- Ghorbani, M.; Noura, S.; Ofstadeh, M.; Zolfigol, M.A.; Soleimani, M.H.; Behbodi, K. *J. Mol. Liq.*, **2015**, *212*, 291-300. <http://dx.doi.org/10.1016/j.molliq.2015.09.024>
- Park, J.H.; Lee, Y.R.; Kim, S.H. *Tetrahedron*, **2013**, *69*(46), 9682-9689. <http://dx.doi.org/10.1016/j.tet.2013.09.021>
- Bose, D.S.; Narsaiiah, A.V. *J. Chem. Res.*, **2001**, *2001*(46), 36-38.
- Narsaiiah, A.V.; Basak, A.K.; Visali, B.; Nagaiah, K. *Synth. Commun.*, **2004**, *34*(16), 2893-2901. <http://dx.doi.org/10.1081/SCC-200026625>
- Lehnert, W. *Tetrahedron*, **1974**, *30*(2), 301-305. [http://dx.doi.org/10.1016/S0040-4020\(01\)91461-9](http://dx.doi.org/10.1016/S0040-4020(01)91461-9)
- Shanthan Rao, P.; Venkataratnam, R.V. *Tetrahedron Lett.*, **1991**, *32*(41), 5821-5822. [http://dx.doi.org/10.1016/S0040-4039\(00\)93564-0](http://dx.doi.org/10.1016/S0040-4039(00)93564-0)
- Bartoli, G.; Beleggia, R.; Giuli, S.; Giuliani, A.; Marcantoni, E.; Mascacesi, M.; Paoletti, M. *Tetrahedron Lett.*, **2006**, *47*(37), 6501-6504. <http://dx.doi.org/10.1016/j.tetlet.2006.07.031>
- Leelavathi, P.; Kumar, S. *J. Mol. Catal. Chem.*, **2005**, *240*, 99-102. <http://dx.doi.org/10.1016/j.molcata.2005.06.026>
- Bartoli, G.; Bosco, M.; Carlone, A.; Dalpozzo, R.; Galzerano, P.; Melchiorre, P.; Sambri, L. *Tetrahedron Lett.*, **2008**, *49*(16), 2555-2557. <http://dx.doi.org/10.1016/j.tetlet.2008.02.093>
- Bao, W.; Zhang, Y.; Wang, J. *Synth. Commun.*, **1996**, *26*(16), 3025-3028. <http://dx.doi.org/10.1080/00397919608004607>
- Liu, S.; Ni, Y.; Yang, J.; Hu, H.; Ying, A.; Xu, S. *Chin. J. Chem.*, **2014**, *32*(4), 343-348. <http://dx.doi.org/10.1002/cjoc.201400025>
- Roy, B.; Roy, A.S.; Panda, A.B.; Islam, S.M.; Chattopadhyay, A.P. *ChemistrySelect*, **2016**, *1*(15), 4778-4784. <http://dx.doi.org/10.1002/slct.201600380>
- Hu, Y.; Yao, N.; Tan, J.; Liu, Y. *Synlett*, **2019**, *30*(6), 699-702. <http://dx.doi.org/10.1055/s-0037-1612076>
- Fu, Z.; Tan, Y.; Zhang, J.; Liao, S.; Su, D.; Chen, H.; Yu, Y.; Peng, J. *Inorg. Chem. Commun.*, **2012**, *15*, 221-224. <http://dx.doi.org/10.1016/j.inoche.2011.10.031>
- Panchenko, V.N.; Matrosova, M.M.; Jeon, J.; Jun, J.W.; Timofeeva, M.N.; Jhung, S.H. *J. Catal.*, **2014**, *316*, 251-259. <http://dx.doi.org/10.1016/j.jcat.2014.05.018>
- Yang, Y.; Yao, H.F.; Xi, F.G.; Gao, E.Q. *J. Mol. Catal. Chem.*, **2014**, *390*, 198-205. <http://dx.doi.org/10.1016/j.molcata.2014.04.002>
- Taher, A.; Lumbiny, B.J.; Lee, I.M. *Inorg. Chem. Commun.*, **2020**, *119*, 108092. <http://dx.doi.org/10.1016/j.inoche.2020.108092>
- Karchgaudhuri, N.; De, A.; Mitra, A.K. *J. Chem. Res.*, **2002**, *2002*, 180-183.
- Steinrück, H.P.; Wasserscheid, P. *Catal. Lett.*, **2015**, *145*(1), 380-397. <http://dx.doi.org/10.1007/s10562-014-1435-x>
- Duc, D.X.; Chung, N.T. *Lett. Org. Chem.*, **2023**, *20*(8), 689-695. <http://dx.doi.org/10.2174/1570178620666230207093953>
- Duc, D.X. *Curr. Organocatal.*, **2023**, *10*(1), 66-72. <http://dx.doi.org/10.2174/2213337210666221214121957>
- Morrison, D.W.; Forbes, D.C.; Davis, J.H., Jr. *Tetrahedron Lett.*, **2001**, *42*(35), 6053-6055. [http://dx.doi.org/10.1016/S0040-4039\(01\)01228-X](http://dx.doi.org/10.1016/S0040-4039(01)01228-X)
- Harjani, J.R.; Nara, S.J.; Salunkhe, M.M. *Tetrahedron Lett.*, **2002**, *43*(6), 1127-1130. [http://dx.doi.org/10.1016/S0040-4039\(01\)02341-3](http://dx.doi.org/10.1016/S0040-4039(01)02341-3)
- Tahmassebi, D.; Wilson, L.J.A.; Kieser, J.M. *Synth. Commun.*, **2009**, *39*(14), 2605-2613. <http://dx.doi.org/10.1080/00397910802663345>
- Xin, X.; Guo, X.; Duan, H.; Lin, Y.; Sun, H. *Catal. Commun.*, **2007**, *8*(2), 115-117. <http://dx.doi.org/10.1016/j.catcom.2006.05.034>
- Mulla, S.A.R.; Sudalai, A.; Pathan, M.Y.; Siddique, S.A.; Inamdar, S.M.; Chavan, S.S.; Reddy, R.S. *RSC Advances*, **2012**, *2*(8), 3525-3529. <http://dx.doi.org/10.1039/c2ra00849a>
- Ranu, B.C.; Jana, R. *Eur. J. Org. Chem.*, **2006**, *2006*(16), 3767-3770. <http://dx.doi.org/10.1002/ejoc.200600335>
- Hou, H.; Li, Z.; Ying, A.; Xu, S. *Youji Huaxue*, **2014**, *34*(7), 1277-1287. <http://dx.doi.org/10.6023/cjoc201402021>
- Pillai, M.K.; Singh, S.; Jonnalagadda, S.B. *Synth. Commun.*, **2010**, *40*(24), 3710-3715. <http://dx.doi.org/10.1080/00397910903531714>
- Yang, X.C.; Jiang, H.; Ye, W. *Synth. Commun.*, **2012**, *42*(3), 309-312. <http://dx.doi.org/10.1080/00397911.2010.523858>
- Zhou, Z.; Sun, Y. *Synth. Commun.*, **2011**, *41*(21), 3162-3168. <http://dx.doi.org/10.1080/00397911.2010.517376>
- Jain, K.; Chaudhuri, S.; Pal, K.; Das, K. *New J. Chem.*, **2019**, *43*(3), 1299-1304. <http://dx.doi.org/10.1039/C8NJ04219E>
- Rupanawar, B.D.; Veetil, S.M.; Suryavanshi, G. *Eur. J. Org. Chem.*, **2019**, *2019*(36), 6232-6239. <http://dx.doi.org/10.1002/ejoc.201900970>
- Panja, S.K.; Dwivedi, N.; Saha, S. *RSC Advances*, **2015**, *5*(80), 65526-65531. <http://dx.doi.org/10.1039/C5RA09036A>
- Ghosh, S.; Jana, C.K. *Org. Biomol. Chem.*, **2019**, *17*(48), 10153-10157. <http://dx.doi.org/10.1039/C9OB02163A> PMID: 31774427
- Kaumanns, O.; Lucius, R.; Mayr, H. *Chemistry*, **2008**, *14*(31), 9675-9682. <http://dx.doi.org/10.1002/chem.200801277> PMID: 18792024