

Ammonium Chloride: An Efficient and Environmentally benign Catalyst for Knoevenagel Condensation of Carbonyl and Active Methylene Compounds

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Received: 30 June 2020;

Accepted: 29 August 2020;

Published online: 7 December 2020;

AJC-20134

In the present study, a rapid, simple and an efficient procedure for the Knoevenagel condensation of various carbonyl and active methylene compounds in ethanol at a moderate temperature in the presence of a catalytic amount of an efficient, environmentally benign and inexpensive ammonium chloride is reported. Simple reaction procedure, economic and ecofriendly catalyst, mild reaction conditions and good to excellent yield of the products are the characteristic features of this study. The non-extractive workup/purification, economic and environmentally benign catalyst make this operationally straightforward procedure affordable for large scale.

Keywords: Active methylene, Ammonium chloride catalyst, Knoevenagel condensation.

INTRODUCTION

Knoevenagel condensation has emerged as an important powerful synthetic tool in the synthesis of fine chemicals [1], hetero-Diels-Alder adducts [2] and various biologically important heterocyclic compounds [3]. Knoevenagel condensations are widely employed for the carbon-carbon bond formations in the synthetic chemistry [4-8]. The literature data revealed that these condensation reactions were performed in the presence of various catalysts/condensing agents like sodium hydroxide [9], pyridine [10,11], piperidine glacial acetic acid [12], ionic liquids [13,14], surfactants [15], zeolites [16], organocatalyst [17] and Lewis acids such as TiCl_4 [18,19], ZnCl_2 [20], $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ [21] and $\text{HClO}_4 \cdot \text{SiO}_2$ [22]. Knoevenagel condensations have also been performed in different solvents [23-26] such as DMF or DMSO in microwave irradiation [27], ultrasound [28] and solid phase [29,30] techniques. In past decades, several reports have been published about the Knoevenagel condensation such as condensation of Meldrum's acid with aromatic aldehyde in presence of ultraviolet light [31], dialkylimidazolium dimethyl phosphates as solvents and catalysts for Knoevenagel condensation reaction [32], magnesium perchlorate

as efficient Lewis acid for Knoevenagel condensation between β -diketones and aldehydes [33], uncatalyzed Knoevenagel condensation in water as a solvent [34] and Knoevenagel condensation catalyzed by novel *N*-methyl morpholine based ionic liquids in water [35]. It is noteworthy that some of these reported methods have limitations, like often high reaction temperature is required to promote the reactions [22,36], using hazardous solvents, high catalyst loading and non-recoverable catalyst.

Therefore, there is a necessary to explore well-designed, cheap and easily available reagents, which will extend the application scope of Knoevenagel condensation reactions in organic synthesis. In this regard, herein the condensation of various aldehydes with active methylene compounds in the presence of ammonium chloride catalyst is reported. The ammonium chloride is an inexpensive, eco-friendly and easily available catalyst. In the literature, it has been reported as an efficient catalyst in various organic reactions such as one-pot synthesis of diindolylmethanes under solvent-free conditions [37], three-component synthesis of 5-iminooxazoline [38], four component synthesis of pyrrolo[3,4-*b*]pyridinones [39] and in Ugi four-component, five-centered reactions [40].

EXPERIMENTAL

Materials and reagents used were of commercially available. All chemicals and reagents used in this research protocol were of analytical grade and employed without further purification. TLC checking was done on glass plates coated with Silica Gel-G and spotting was done using iodine and UV lamp. The newly synthesized compounds were purified by column chromatography wherever needed. Melting points are uncorrected and were determined in open capillary tubes in the sulfuric acid bath. FT-IR spectra were obtained with a Shimadzu 8000 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian spectrometer.

Synthesis of Knoevenagel condensation product (3a-j):

A mixture of an aromatic aldehyde (**1**, 10 mmol), active methylene compound **2** (10 mmol) and catalyst NH_4Cl (10 mol %) in ethanol (10 mL) was refluxed for 2 h. The formation of the products was monitored by TLC. After completion of the reaction as indicated by TLC, the mixture was cooled to room temperature and filtered. The filtrate was concentrated to obtain the crude product, which was purified and recrystallized from ethanol and water mixture to obtain pure products in high yields (**Scheme-I**).

Ethyl-2-cyano-3-phenylacrylate (3a): White crystalline solid; m.p.: 49-50 °C; IR (KBr, ν_{max} , cm^{-1}): 2924, 2224, 1726, 1604, 1529, 1452, 1367, 1265, 1199, 1093, 1014, 954, 767, 684. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 1.70 (t, $J = 7.1$, 3H), 4.67 (q, $J = 7.1$ Hz, 2H), 7.84 (t, $J = 7.3$ Hz, 2H), 8.30 (t, $J = 7.3$ Hz, 2H), 8.55 (s, 1H).

Ethyl-3-(4-chlorophenyl)-2-cyanoacrylate (3b): White solid; m.p.: 88-89 °C; IR (KBr, ν_{max} , cm^{-1}): 2985, 2225, 1739, 1600, 1452, 1373, 1242, 1047, 933, 842, 788, 634. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 1.38 (t, $J = 7.2$ Hz, 3H), 4.38 (q, $J = 7.2$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.93 (d, $J = 8.5$ Hz, 2H), 8.18 (s, 1H). ^{13}C NMR (300 MHz; CDCl_3 , δ ppm): 14.26, 62.03, 103.37, 115.94, 129.50, 132.02, 139.49, 153.37, 161.87.

Ethyl-2-cyano-2-*p*-tolylacrylate (3c): Colourless solid; m.p.: 91-92 °C; IR (KBr, ν_{max} , cm^{-1}): 3100, 2850, 2210, 1710, 1600, 1460, 1370, 1270, 1200, 1100. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 1.40 (t, $J = 7.06$, 3H), 2.43 (s, 3H), 4.38 (q, $J = 7.06$, 2H), 7.26 (d, $J = 7.69$, 2H), 7.86 (d, $J = 8.14$, 2H), 8.21 (s, 1H).

Ethyl-2-cyano-3-(4-hydroxyphenyl)acrylate (3d): Yellow solid; m.p.: 169-171 °C; IR (KBr, ν_{max} , cm^{-1}): 3414, 2235, 1716, 1579, 1512, 1402, 1271, 1207, 1172, 1055, 910, 819, 734, 648; ^1H NMR (300 MHz; CDCl_3 , δ ppm): 1.40 (t, $J = 7.1$ Hz, 3H), 2.93 (s, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 7.96 (d, $J = 8.8$ Hz, 2H), 8.30 (s, 1H).

Ethyl-2-cyano-3-(4-nitrophenyl)-2-propenoate (3e): Yellow solid; m.p.: 169-170 °C; IR (KBr, ν_{max} , cm^{-1}): 3451, 2991, 2226, 1718, 1612, 1590, 1510, 1342, 1262, 1205, 1196, 865,

734, 648. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 1.32 (t, 3H, $J = 7.1$ Hz), 4.33 (q, 2H, $J = 7.11$), 8.24 (d, $J = 8.8$ Hz, 2H), 8.40 (d, $J = 9.0$ Hz, 2H), 8.55 (s, 1H).

Ethyl-2-cyano-3-(4-methoxyphenyl)acrylate (3f): Yellow crystals; m.p.: 79-80 °C; IR (KBr, ν_{max} , cm^{-1}): 2990, 2916, 2215, 1710, 1584, 1561, 1513, 1431, 1262, 1211, 1184, 1127, 1089, 1017, 837. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 1.44 (t, 3H, $J = 7.1$ Hz), 3.92 (s, 3H), 4.38 (q, 2H, $J = 7.1$ Hz), 6.97 (d, 2H, $J = 9.0$ Hz), 8.02 (d, $J = 9.0$ Hz, 2H), 8.20 (s, 1H). ^{13}C NMR (300 MHz; CDCl_3 , δ ppm): 14.2, 55.6, 62, 99.36, 114.7, 116.2, 124.37, 133, 154.4, 163.13, 163.79.

2-Benzylidenemalononitrile (3g): White solid; m.p.: 80-81 °C; IR (KBr, ν_{max} , cm^{-1}): 3817, 3722, 3307, 2934, 2540, 2302, 2221, 2074, 1922, 1783, 1583, 1413, 1410, 1288, 1210, 1090, 933, 774, 732, 622. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 7.52 (t, $J = 7.7$ Hz, 1H), 7.64 (t, $J = 7.4$ Hz, 2H), 7.79 (s, 1H), 7.92 (d, $J = 7.5$ Hz, 2H).

2-(4-Chlorobenzylidene)malononitrile (3h): White solid; m.p.: 90-91 °C; IR (KBr, ν_{max} , cm^{-1}): 3807, 3724, 3317, 3032, 2935, 2584, 2303, 2225, 2075, 1928, 1788, 1585, 1419, 1410, 1290, 1219, 1095, 937, 779, 704, 617; ^1H NMR (300 MHz; CDCl_3 , δ ppm): 7.53 (d, $J = 8.0$ Hz, 2H), 7.74 (s, 1H), 7.84 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (300 MHz; CDCl_3 , δ ppm): 83.62, 111.63, 113.25, 129.28, 130.58, 132.17, 140.94, 158.01.

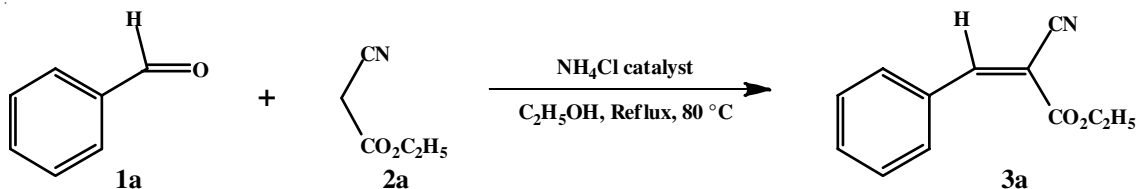
2-(4-Methylbenzylidene)malononitrile (3i): White solid; m.p.: 135-136 °C; IR (KBr, ν_{max} , cm^{-1}): 3827, 3712, 3300, 2928, 2530, 2302, 2201, 2064, 1922, 1783, 1583, 1418, 1425, 1290, 1210, 1098, 933, 778, 732, 628. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 2.46 (s, 3H), 7.33 (t, $J = 8.0$ Hz, 2H), 7.72 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 2H).

2-(2-Nitrophenyl)-3-phenylacrylonitrile (3j): White solid; m.p.: 106-115 °C; IR (KBr, ν_{max} , cm^{-1}): 3098, 2936, 2845, 2506, 2401, 2204, 1930, 1900, 1802, 1502, 1511, 1332, 1204, 1087, 1028, 901, 840, 810, 742, 630. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 7.51 (t, 2H), 7.69 (s, 1H), 7.88 (d, $J = 7.9$ Hz, 2H), 7.95 (s, $J = 7.9$ Hz, 2H), 8.31 (t, $J = 7.9$ Hz, 2H).

3-(4-Chlorophenyl)-2-(2-nitrophenyl)acrylonitrile (3k): White solid; m.p.: 140-142 °C; IR (KBr, ν_{max} , cm^{-1}): 3099, 2926, 2835, 2596, 2441, 2214, 1940, 1911, 1817, 1519, 1510, 1342, 1203, 1097, 1008, 910, 858, 828, 750, 669. ^1H NMR (300 MHz; CDCl_3 , δ ppm): 7.51 (d, $J = 6.8$ Hz, 2H), 7.63 (s, 1H), 7.87 (m, 4H), 8.31 (d, $J = 6.8$ Hz, 2H). ^{13}C NMR (300 MHz; CDCl_3 , δ ppm): 110.08, 116.94, 124.44, 126.80, 129.57, 130.93, 131.30, 137.80, 140.24, 143.95, 148.03.

RESULTS AND DISCUSSION

Initially, the condensation of benzaldehyde with ethyl cyanoacetate was chosen as the model reaction to optimize conditions (**Scheme-I**). It was found that in the presence of ammonium chloride catalyst (10 mol%) and aqueous ethanol



Scheme-I: Ammonium chloride catalyzed Knoevenagel condensation reaction

solvent system a very high yield (98%) of corresponding product was obtained in just 30 min. The results are summarized in Table-1. When the model reaction (**Scheme-I**) was performed in the presence of catalysts like piperidinium acetate and pyridinium *p*-toluene sulfonate (Table-1, entries 1-6) very less yield of the desired product was obtained after longer reaction time. The reaction was further explored as per the literature procedure with the catalysts KSF clay [41] SbCl₃ [42], ZrO₂ [43] and Yb[OTf]₃ [44] (Table-1, entries 7-10), however, this resulted in lowers of the desired product. In subsequent optimization of the model reaction, the reaction in the presence of 10 mol% of ammonium chloride catalyst in aqueous ethanol solvent system was carried (Table-1, entry 11). Due to high reactivity of the catalyst the respective product was obtained in excellent yield. Therefore, it was concluded that ammonium chloride catalyst (10 mol%) and aqueous ethanol is the best reaction media for the condensation of benzaldehyde (10 mmol) with ethyl cyanoacetate (10 mmol).

TABLE-1
COMPARISON OF THE CATALYTIC ACTIVITY OF
NH₄Cl WITH OTHER CATALYST^a

Entry	Catalyst (10 mol %)	Time (min)	Yield ^b (%)
1	Piperidinium acetate (ethanol solvent)	60	60
2	Piperidinium acetate (glycerol solvent)	60	65
3	Piperidinium acetate (PEG600 solvent)	60	60
4	Pyridinium <i>p</i> -toluene sulfonate (ethanol solvent)	60	65
5	Pyridinium <i>p</i> -toluene sulfonate (glycerol solvent)	60	50
6	Pyridinium <i>p</i> -toluene sulfonate (PEG600 solvent)	60	55
7	KSF clay	180	75 [41]
8	SbCl ₃	280	80 [42]
9	ZrO ₂	210	90 [43]
10	Yb[OTf] ₃	60	75 [44]
11	NH ₄ Cl catalyst (ethanol solvent)	30	98

^aReaction conditions: Benzaldehyde (1mmol), ethyl cyanoacetate (1 mmol), NH₄Cl catalyst (10 mol%) and aqueous ethanol under reflux condition at 80 °C; ^bYields of the isolated products.

In continuation of our efforts for the optimization of the model reaction, the same reaction in various solvents was monitored using NH₄Cl catalyst under the reflux condition at 80 °C. It is observed that the reaction gave only 20% of the desired product in the absence of solvent (Table-2, entry 1). The usage of water as solvent (Table-2, entry 2) also not significantly enhanced the yield of the respective product. The reaction using ethanol as solvent at room temperature (Table-2, entry 3) was also performed and found to yield 60% of the corresponding product. To improve the yield of the desired product, the reaction was carried out in several solvents such ethylene glycol, DMF, acetic acid, acetonitrile, THF and DMS (Table-2, entries 4-9), however not much improved in the yield of the desired product. It was found that ethanol under reflux afforded the desired products in higher yield (98%) in shorter reaction time (Table-2, entry 10).

The effect of quantity of NH₄Cl catalyst on the speed of the reaction and yield of the product was also studied. When

TABLE-2
OPTIMIZATION OF REACTION
CONDITIONS USING VARIOUS SOLVENTS

Entry	Solvent	Time (min)	Conditions	Yield ^a (%)
1	No solvent	160	Reflux	20
2	Ethanol	120	R.T	60
3	Water	120	Reflux	50
4	Ethylene glycol	120	Reflux	70
5	DMF	60	Reflux	60
6	Acetic acid	60	Reflux	75
7	Acetonitrile	60	Reflux	70
8	THF	60	Reflux	60
9	DMS	60	Reflux	60
10	Ethanol	30	Reflux	98

^aReaction conditions: Benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), NH₄Cl-catalyst (10 mol%) under reflux condition at 80 °C.

^bYields of the isolated products.

the model reaction was carried out in aqueous ethanol without NH₄Cl as catalyst, the reaction was found to be sluggish and resulted in a low yield of the product. The optimum amount of NH₄Cl required in the above reaction was also studied by changing the amount of catalyst from 0, 2.5, 5, 8, 10 and 15 mol% in aqueous ethanol. The corresponding product was obtained in 10, 60, 70, 90, 98 and 88% yield, respectively. The best result was obtained when 10 mol% of catalyst NH₄Cl was used. The results are summarized in Table-3.

TABLE-3
OPTIMIZATION OF REACTION CONDITIONS
USING DIFFERENT AMOUNTS OF CATALYST NH₄Cl

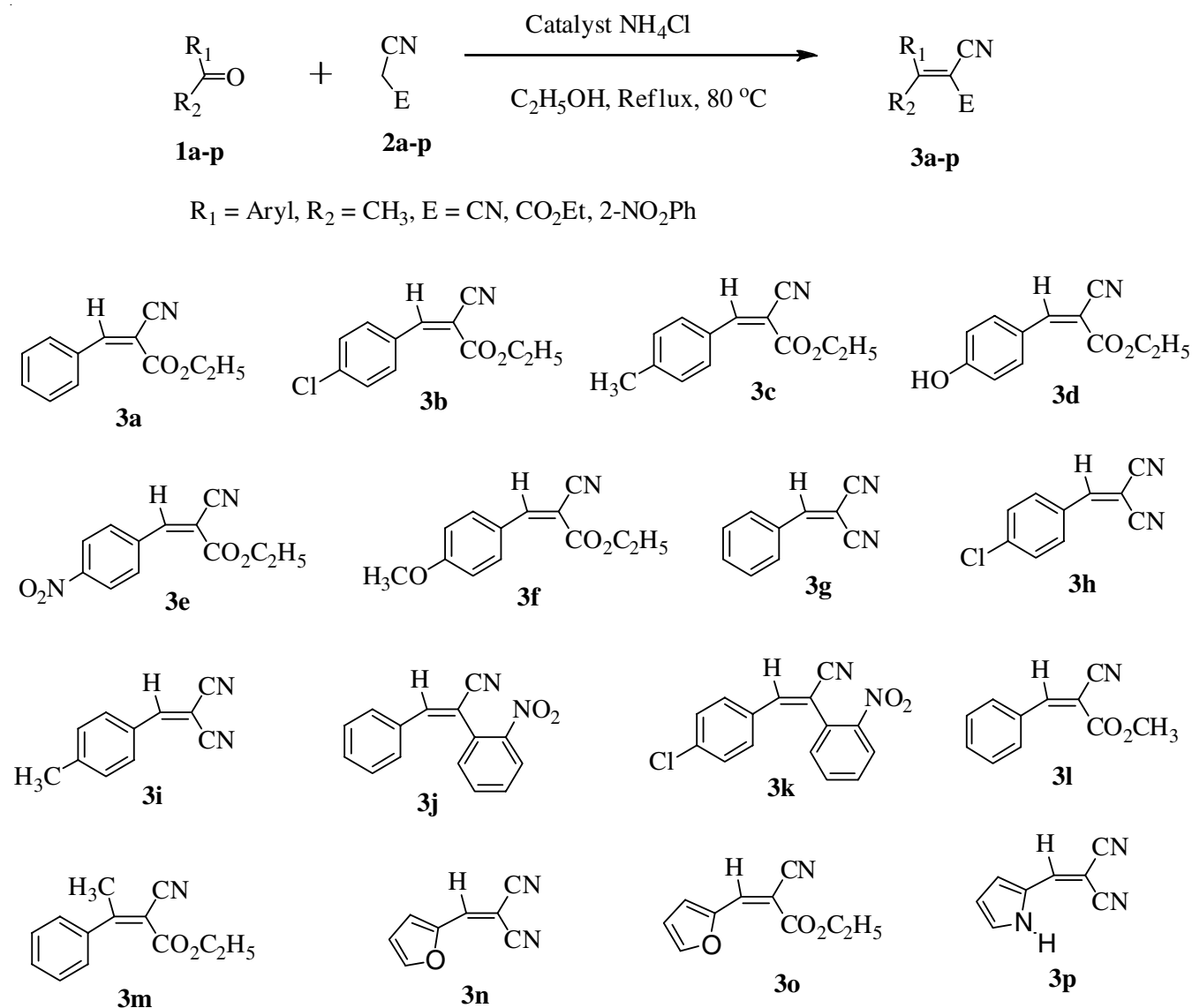
Entry	Catalyst (mol %)	Time (min)	Yield ^a (%)
1	0	540	10
2	2.5	60	60
3	5	30	70
4	8	30	90
5	10	30	98
6	15	30	88

^aReaction conditions: Benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol) NH₄Cl-catalyst and aqueous ethanol under reflux condition at 80 °C. ^bYields of the isolated products.

In the light of the above results and to show the generality of this reaction, the optimized reaction conditions were applied to a variety of benzaldehydes and active methylene compounds (**Scheme-II**) and the results are summarized in Table-4. It is worth to mention that in all cases, the reaction proceeds smoothly with 10 mol% NH₄Cl in ethanol. It was observed that the condensation of aldehydes with electron-withdrawing groups such as -Cl and NO₂ on the aromatic ring, with active methylene compounds, can be carried out in relatively less time than with electron-donating groups such as -CH₃, OH and -OCH₃.

Conclusion

In this work, a convenient, simple and high yield method for the Knoevenagel condensation of various aromatic aldehydes and active methylene compounds in the presence of readily available and an environmentally friendly, NH₄Cl catalyst is developed. Significant advantages of this study are reasonably simple experimental workup procedure, mild reaction condition, ease of product isolation, good to an excellent yield of the

Scheme-II: Knoevenagel condensation reaction products (3a-p) catalyzed by NH_4Cl TABLE-4
KNOEVENAGEL CONDENSATION CATALYZED BY NH_4Cl ^{a,b,c}

Entry	R ₁	R ₂	E	Product	Time (min)	Yield ^b (%)
1	C ₆ H ₅	H	CO ₂ C ₂ H ₅	3a	35	90
2	4-Cl-C ₆ H ₄	H	CO ₂ C ₂ H ₅	3b	30	94
3	4-CH ₃ -C ₆ H ₄	H	CO ₂ C ₂ H ₅	3c	35	96
4	4-OH-C ₆ H ₄	H	CO ₂ C ₂ H ₅	3d	37	90
5	4-NO ₂ -C ₆ H ₄	H	CO ₂ C ₂ H ₅	3e	40	88
6	4-OCH ₃ -C ₆ H ₄	H	CO ₂ C ₂ H ₅	3f	30	95
7	C ₆ H ₅	H	CN	3g	30	98
8	4-Cl-C ₆ H ₄	H	CN	3h	30	90
9	4-CH ₃ -C ₆ H ₄	H	CN	3i	35	88
10	C ₆ H ₅	H	2-NO ₂ -C ₆ H ₄	3j	30	90
11	4-Cl-C ₆ H ₄	H	2-NO ₂ -C ₆ H ₄	3k	30	90
12	C ₆ H ₅	CH ₃	CO ₂ CH ₃	3l	35	94
13	C ₆ H ₅	CH ₃	CO ₂ C ₂ H ₅	3m	35	90
14	C ₄ H ₃ O (Furyl)	H	CN	3n	40	90
15	C ₄ H ₃ O (Furyl)	H	CO ₂ C ₂ H ₅	3o	40	88

^aReaction conditions: Carbonyl compounds (1 mmol), activated methylene compound (1 mmol), NH_4Cl -catalyst (10 mol%) and aqueous ethanol under reflux condition at 80 °C. ^bYields of the isolated products.

products, short reaction time, high atom economy by using non-hazardous solvents and catalytic amount of catalyst. All these merits make the present methodology a valid contribution to the existing methods of Knoevenagel condensation of aromatic aldehydes with active methylene compounds.

ACKNOWLEDGEMENTS

This work was supported by the Dean of Scientific Research, King Khalid University, Saudi Arabia for the General Research Project under grant number [G.P.R. 362/42].

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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