Green and efficient Knoevenagel condensation catalysed by a DBU based ionic liquid in water

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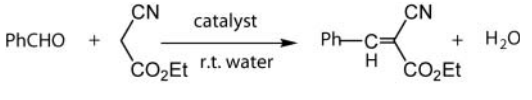
An efficient, clean and facile protocol for the Knoevenagel condensation of aromatic aldehydes with active methylene compounds catalysed by task specific ionic liquid 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate in an aqueous medium has been developed. The reactions proceed at room temperature and high to excellent yields were afforded. The work-up procedure is very simple. The ionic liquid could be recycled for 10 runs without noticeably loss of its catalytic activity.

Keywords: DBU, [DBU]Ac], ionic liquid, Knoevenagel condensation, aromatic aldehydes, recyclability.

The Knoevenagel condensation is one of most important C=C double bond forming reactions in organic chemistry. The condensation products, the α, β-unsaturated nitriles and their derivatives, have been widely used in the preparation of complex and novel heterocyclic compounds of biologically significance[1] which have extensive applications in cosmetics, perfumes and several therapeutic drugs[2]. This reaction is generally catalysed by bases or acids mainly including DMAP[3], N-methylpiperazine[4], potassium fluoride mixture[5], guanidines[6], ethylene diamine[7,8], I_2/K_2CO_3[9], perfluoroalkylated pyridine[10], SmI_3[11], $ZnCl_2$[12], $CuCl_2$[13], $LaCl_3$[14], sulfate-ion promoted zirconia solid acid[15], $NbCl_5$[16] and ionic liquids[17]. Many of these procedures have drawbacks such as long reaction time, harsh reaction conditions, stoichiometric amount of catalysts, and large amounts of organic solvent as the reaction medium. Thus, there is still a need for new, mild and efficient methodologies for Knoevenagel condensations.

1,8-Diazabicylco[5.4.0]-undec-7-ene (DBU) was found to be superior to other tertiary amines as a catalyst. DBU's nucleophilic nature has also been investigated over the past decades.[18] Based on this unusual properties of DBU, Aggarwal[19] and Kim[20] reported DBU as catalyst for Baylis–Hillman reaction and aza-Michael addition, respectively. Recently, Kakade *et al*. investigated the use of DBU as catalyst for Knoevenagel reaction of 2-chloroquinoline-3-carbaldehyde with ethyl cyanoacetate under ultrasonic irradiation.[21] Encouraged by this, we tested the reaction of benzaldehyde with ethyl cyanocetate catalysed by 20 mol% amount of DBU in water (Table 1, entry 7) and we found that a 93% yield of the condensation product was obtained within 2 hours. However, using DBU as catalyst has some problems since it could not be reused and has an unpleasant odour during the operation of this process. This also exists with other organic bases as promoters for synthetic transformation. On the other hand, ionic liquids, due to their unique properties of good solvating ability, negligible vapour pressure, nonflammability, easy product separation as well as efficient recyclability have been widely used as catalysts as well as reaction medium in organic chemistry.[22–24] 1,8-Diazabicyclo[5.4.0]-undec-7-en-8-ium acetate ([DBU][Ac]) has been developted and was successfully used as catalyst for aza-Michael addition.[25] Thus, we wanted to test the efficiency of [DBU][Ac] as catalyst for Knoevenagel condensation of aromatic aldehydes with active methylene compounds.

Table 1 Results of DBU and varying the amounts of [DBU][Ac] in the aqueous Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate at room temperature



Entry	Catalysts/mol%	Time/h	Yields[a]/%
1	[DBU][Ac] (1)	3	59
2	[DBU][Ac] (5)	3	73
3	[DBU][Ac] (20)	2	95
4	[DBU][Ac] (50)	2	94
6	–	10	36
7	DBU (20)	2	93

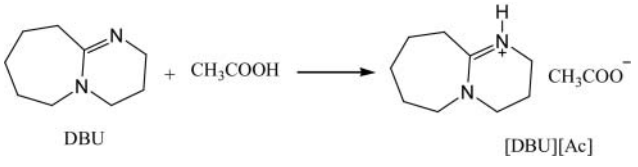
[a] Isolated yields of products.

Results and discussion

Ionic liquid 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium lactate [DBU][Ac] was synthesised by simple neutralisation of DBU with acetic acid (Scheme 1)[25]. Then we examined [DBU][Ac] as catalyst for the reaction of benzaldehyde with ethyl cyanoacetate in water at room temperature. An excellent yield of the desired product was obtained (Table 1, entry 3). The result is comparable with that obtained from the reaction catalysed by parent catalyst DBU. Bhuyan *et al.* published a method for the Knoevenagel reaction in aqueous medium without any catalyst.[26] However, the method was substrate-selective and the aqueous reaction of benzaldehyde with ethyl cyanoacetate in the absence of [DBU][Ac] is very slow with a low yield obtained (Table 1, entry 6). The result indicated that the ionic liquid [DBU][Ac] played an important role as a catalyst during the reaction process.

To find a optimal loading amount of catalyst for the model reaction of benzaldehyde and ethyl cyanoacetate, the amount of [DBU][Ac] was reduced from 0.5 equiv to 0.01 equiv. The results are collected in Table 1. The reactivity for lower loading of [DBU][Ac] (0.01 equiv) decreased. When the amount of [DBU][Ac] was increased from 20 to 50 mol%, the expected improvement in yield of electrophilic alkene was not observed (Table 1, entries 1–4). Thus, we chose 0.2 equiv as the optimal amount of catalyst for further examinations.

With the best catalytic system in hand, we investigated the Knoevenagel reaction of various aromatic aldehydes with



Scheme 1 Synthesis of ionic liquid [DBU][Ac].

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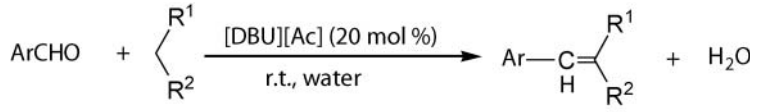
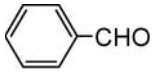
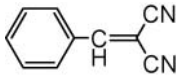
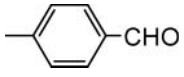
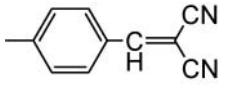
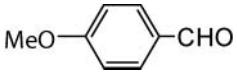
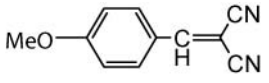
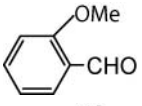
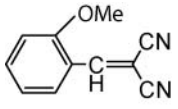
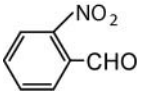
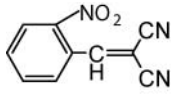
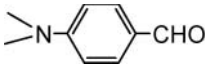
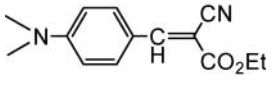
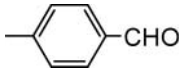
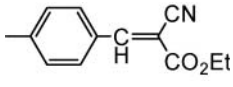
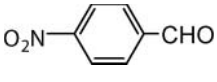
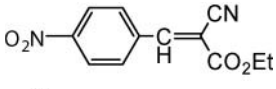
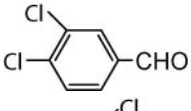
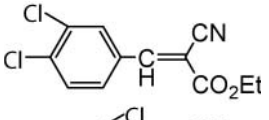
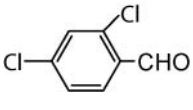
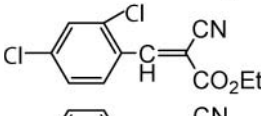
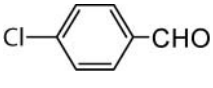
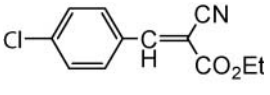
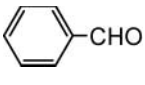
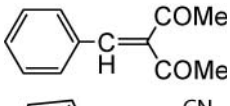
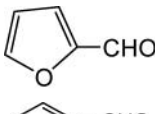
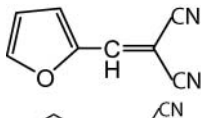
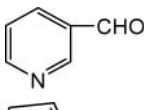
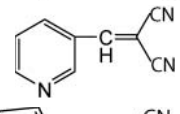
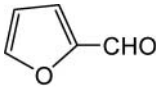
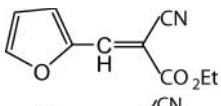
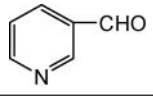
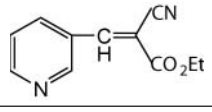
Table 2 Results of Knoevenagel condensation between various aromatic aldehydes and methylene active compounds at room temperature in aqueous media[c]



Entry	Ar	R^1	R^2	Time/h	Products	Yields[a]/%
1		CN	CN	0.3		93
2		CN	CN	0.3		94
3		CN	CN	0.3		94
4		CN	CN	0.3		90
5		CN	CN	0.2		88
6[d]		CN	CO_2Et	6		96
7		CN	CO_2Et	4		95
8		CN	CO_2Et	1		90
9		CN	CO_2Et	3		82
10		CN	CO_2Et	2		75
11		CN	CO_2Et	1.5		95
12[d]		COMe	COMe	10		63[b]
13		CN	CN	1		86
14		CN	CN	1		96
15		CN	CO_2Et	3		92
16		CN	CO_2Et	3		94

[a] Isolated yields of desired products [b] Starting materials detected
[c] Reaction conditions: aromatic aldehydes (1 mmol), active methylene compounds (1mmol) stirred in water (1mL) with 20 mol% [DBU][Ac] as catalyst at room temperature
[d] Reactions at 60 °C.

malononitrile and ethyl cyanoacetate. The results are shown in Table 2. A variety of structurally diverse aromatic aldehydes reacted favorably with active nucleophilic reagents to give the desired products in good to excellent yields. The products were isolated by simple filtration without further purification. All products were verified by melting point, ^{1}H NMR and ^{13}C NMR spectroscopy which were in agreement with other published data.

When malononitrile was treated with aromatic aldehydes bearing electron donating or withdrawing groups, the reactions proceeded within short time to give very high yields (Table 2, entries 1–5). It is notable that electron-donating or electron-withdrawing substituents on the aromatic rings have less effect on Knoevenagel reaction presumably due to the strong activity of acidic malononitrile. However, the aromatic aldehydes carrying electron-donating groups reacted slowly with ethyl cyanoacetate, although the corresponding yields were excellent when the reaction time was prolonged (Table 2, entries 6 and 7). It can also been seen from Table 2 that more sluggish methylene compounds, β-dicarbonyl compound do not react completely and moderate yields were obtained (Table 2, entry 12). Hence the order for reaction rate as well as efficiency of Knoevenagel reaction is as follows: malononitrile>ethyl cyanoacetate>β-dicarbonyl compound, which is accordance with the acidic activity of three substances. In addition, Knoevenagel condensation of hetero aromatic aldehydes such as 2-furaldehyde and 3- pyridinecarboxaldehyde with active methylene compounds also proceeded smoothly at room temperature (Table 2, entries 13–16). Note that all products obtained had the *E*-geometry exclusively and no *Z*-geometrical isomers and subsequent Michael adducts are detected.

In order to demonstrate the industrial applicability of this methodology, the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was carried out on a larger scale (100 mmol) in water (100 mL). The reaction was completed in 2 h. An excellent yield of 97% for the condensational product was achieved. On the same scale, the recyclability of catalytic system was investigated using the same reaction as model reaction. Upon the completion of the reaction, the highly pure product was obtained by filtration without further separation, while the remaining aqueous medium containing [DBU][Ac] was reused directly without additional recovery. As shown in Fig. 1, the catalytic system of [DBU][Ac] in water can be reused 10 times without noticeable loss of its activity.

Conclusion

In summary, we have established a simple, mild and efficient methodology for the Knoevenagel condensation between aromatic aldehydes and methylene compounds at ambient temperature in water with ionic liquid [DBU][Ac] as the catalyst. This protocol has notable advantages, such as high product yields, aqueous reaction medium, ease of work-up, reuse of ionic liquid on large scale, which make this method more efficient and clean with an industrial potential.

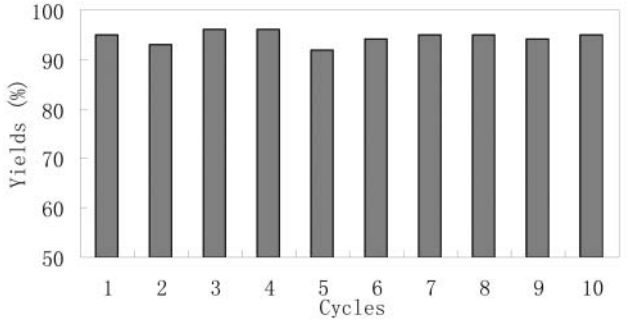


Fig. 1 Reuse of catalyst for Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate (100 mmol) in 100 mL water.

Experimental

All chemicals were purchased from Aldrich or Fluka. ^{1}H and ^{13}C NMR were recorded on a Bruker Avance DPX 400 spectrometer at 400 MHz and 100 MHz in $CDCl_3$ and D_2O respectively. Chemical shifts were reported in parts per million (δ), relative to the internal standard of tetramethylsilane (TMS). Melting points were determined using YRT-3 apparatus and were not corrected. Elemental analysis was carried out on a Carlo Erba 1160. All reactions were monitored by TLC. All condensation products were characterised by NMR analysis and melting points.

General procedure for preparation of ionic liquid [DBU][Ac][25]

6 mmol of DBU was added to a 50 mL three-necked flask, actetic acid (6 mmol) was then added dropwise at the temperature of ⩽5 °C cooled by an ice bar. After dropwise addition, the ice bar was removed and the reaction mixture was stirred at room temperature for 24 h. The oil residue was dried *in vacuo* at 60 °C for 24 h to afford [DBU][Ac] as a light yellow, viscous liquid. [DBU][Ac]

^{1}H NMR (400 MHz, D_2O): δ = 3.50–3.48 (m, 2H, 9-H), 3.44–3.41 (m, 2H, 11-H), 3.23–3.20 (m, 2H, 2-H), 2.75–2.72 (m, 2H, 6-H), 1.89–1.83 (m, 2H, 10-H), 1.68–1.51 (m, 6H, 3-H, 4-H, 5-H), 1.63 (s, 3H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ = 174.4, 165.2, 53.1, 47.9, 37.8, 31.2, 28.6, 26.5, 25.1, 24.0, 19.5; Anal. Calcd for [DBU][Ac] C, 62.10; H, 9.55; N, 13.11; O, 15.24. Found C, 62.23; H, 9.50; N, 13.20; O, 15.07%.

Typical experimental process for the Knoevenagel condensation

Benzaldehyde (1 mmol) and ethyl cyanoacetate (1 mmol) were mixed together in the presence of 20 mol% [DBU][Ac] in 1 mL water, then stired at room temperature. Upon the completion of the reaction (monitored by TLC), the mixture was filtrated and the solid, dried *in vacuo* at 60 °C for 10 h, which gave the desired product in high purity that did not need further purification. The residue solution containing [DBU][Ac] was reused for subsequent reactions. The product was analysed by melting point, ^{1}H NMR and ^{13}C NMR.

Data for condensation products

2-(Phenylmethylene)-malononitrile (Table 2, entry 1): White solid; m.p. 79–80 °C (lit.[27]80–81 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 7.91 (d, 2H, *J* = 7.6 Hz, ArH), 7.79 (s, 1H, C=CH), 7.64 (t, 1H, *J* = 7.6 Hz, ArH), 7.27 (t, 2H, *J* = 7.6 Hz, ArH), 7.27 (t, 2H, *J* = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 160.0, 134.6, 130.9, 130.7, 129.6, 113.7, 112.5, 82.7.

2-(4-Methylphenylmethylene)malononitrile (Table 2, entry 2): White solid; m.p. 134–135 °C (lit.[29]132–133 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 7.82 (d, 2H, *J* = 8 Hz, ArH), 7.73 (s, 1H, C=CH), 7.34 (d, 2H, *J* = 8 Hz, ArH), 2.46 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 159.8, 146.4, 130.9, 130.3, 128.4, 114.0, 112.8, 81.1, 22.0.

2-(4-Methyoxyphenylmethylene)malononitrile (Table 2, entry 3): Yellow solid; m.p. 110–112 °C(lit.[27]110–111 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 7.91 (d, 2H, *J* = 8.8 Hz, ArH), 7.66 (s, 1H, C=CH), 7.01 (d, 2H, *J* = 8.8 Hz, ArH), 3.92 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 164.8, 158.9, 133.4, 123.9, 115.1, 114.4, 113.3, 78.4, 55.8.

2-(2-Methyoxyphenylmethylene)malononitrile (Table 2, entry 4): Yellow solid; m.p. 82–84 °C(lit.[34]84–86 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.31 (s, 1H, C=CH), 8.18 (d, 1H, *J* = 7.6 Hz, ArH), 7.62–7.57 (m, 1H, ArH), 7.08 (t, 1H, *J* = 7.6 Hz, ArH), 6.99 (d, 1H, *J* = 8.8 Hz, ArH), 3.93 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 158.9, 154.4, 136.5, 128.8, 121.1, 120.1, 114.3, 112.9, 111.4, 81.2, 55.9.

2-(2-Nitrophenylmethylene)malononitrile (Table 2, entry 5): Yellow solid; m.p. 136–138 °C(lit.[31]134–136 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.46 (s, 1H, C=CH), 8.36 (d, 1H, *J* = 8 Hz, ArH), 7.91–7.88 (m, 1H, ArH), 7.84–7.80 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 158.9, 146.7, 134.9, 133.4, 130.4, 126.6, 125.8, 112.2, 110.9, 88.4.

Ethyl (E)-2-cyano-3-(4-N,N-dimethylphenyl)-2-propenoate (Table 2, entry 6): Yellow solid; m.p. 124–125 °C(lit.[30]126–127 °C); ^{1}H NMR

(400 MHz, $CDCl_3$) (ppm): 8.07 (s, 1H, C=CH), 7.93 (d, 1H, J = 8.8 Hz, ArH), 6.69 (d, 2H, J = 8.8 Hz, ArH), 4.33 (q, 2H, J = 7.2 Hz, CH_2), 1.37 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 184.2, 154.4, 153.4, 133.9, 119.2, 117.5, 111.3, 93.7, 61.7, 39.9, 14.2.

Ethyl (E)-2-cyano-3-(4-methylphenyl)-2-propenoate (Table 2, entry 7): White solid; m.p. 93–94 °C(lit.[28]92–93 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.22 (s, 1H, C=CH), 7.90 (d, 2H, J = 8 Hz, ArH), 7.30 (d, 2H, J = 8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 162.7, 155.0, 144.6, 131.2, 130.0, 128.8, 115.7, 101.4, 62.5, 21.8, 14.1.

Ethyl (E)-2-cyano-3-(4-nitrophenyl)-2-propenoate (Table 2, entry 8): Pale yellow solid; m.p. 168–171 °C(lit.[28]169–170 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.35 (d, 2H, J = 8.4 Hz, ArH), 8.31 (s,1H, C=CH), 8.14 (d, 2H, J = 8.4 Hz, ArH), 4.43 (q, 2H, J = 7.2 Hz, CH_2), 1.42 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 161.4, 151.7, 149.6, 136.9, 131.1, 124.3, 114.5, 107.3, 63.3, 14.1.

Ethyl (E)-2-cyano-3-(3,4-dichlorophenyl)-2-propenoate (Table 2, entry 9): White solid; m.p. 128–130 °C(lit.[32]124–126 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.15 (s, 1H, C=CH), 8.01 (d, 1H, J = 1.6 Hz, ArH), 7.91–7.88 (m, 1H, ArH), 7.59 (d, 1H, J = 8.4 Hz, ArH), 4.40 (q, 2H, J = 7.2 Hz, CH_2), 1.40 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 161.7, 151.8, 137.5, 133.7, 132.6, 131.2, 131.1, 129.2, 114.7, 104.7, 62.9, 14.0.

Ethyl (E)-2-cyano-3-(2,4-dichlorophenyl)-2-propenoate (Table 2, entry 10): White solid; m.p. 81–82 °C(lit.[33]79–80 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.61 (s, 1H, C=CH), 8.20 (d, 1H, J = 8.8 Hz, ArH), 7.53 (d, 1H,J = 1.6 Hz, ArH), 7.41–7.39 (m, 1H, ArH), 4.40 (q, 2H, J = 7.2 Hz, ArH), 1.41 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 161.5, 149.6, 139.3, 137.2, 130.4, 130.2, 128.2, 127.9, 114.6, 106.3, 63.0, 14.0.

Ethyl (E)-2-cyano-3-(4-chlorophenyl)-2-propenoate (Table 2, entry 11): White solid; m.p. 89–90 °C(lit.[28]91–92 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.20 (s, 1H, C=CH), 7.94 (d, 2H, J = 8.8 Hz, ArH), 7.48 (d, 2H, J = 8.8 Hz, ArH), 4.39 (q, 2H, J = 7.2 Hz, CH_2), 1.40 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 162.2, 153.4, 139.5, 132.2, 129.8, 129.6, 115.2, 103.4, 62.8, 14.1.

3-Benzylidene-2,4-pentanedione (Table 2, entry 12): Pale yellow solid; m.p. 184–186 °C(lit.[30]185–188 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 7.47 (s, 1H, C=CH), 7.37 (m, 5H, ArH), 2.40 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 200.6, 191.5, 137.8, 134.8, 127.8, 125.6, 124.6, 123.9, 26.6, 21.4.

2-(2-Furylmethylene)malononitrile (Table 2, entry 13): Pale yellow solid; m.p. 68–69 °C(lit.[27]68–69 °C);; ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 7.81 (d, 1H, J = 1.6Hz, furyl), 7.52 (s, 1H, C=CH), 7.37 (d, 1H, J = 3.6Hz, furyl), 6.73–6.71 (m, 1H, furyl); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 149.6, 147.9, 143.0, 123.6, 114.4, 113.8, 112.6.

2-(3-Pyridylmethylene)malononitrile (Table 2, entry 14): White solid; m.p. 80–83 °C(lit.[35]78–80 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.89 (d, 1H, J = 2 Hz, pyridyl), 8.83 (d, 1H, J = 3.6 Hz, pyridyl), 8.49–8.47 (m 1H, pyridyl), 7.55–7.52 (m, 1H, pyridyl); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 158.5, 154.6, 152.3, 135.6, 126.9, 124.2, 112.9, 111.9, 85.5.

Ethyl (E)-2-cyano-3-(2-furyl)-2-propenoate (Table 2, entry 15): White solid; m.p. 91–92 °C(lit.[28]93–94 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.02 (s, 1H, C=CH), 7.76 (d, 1H, J = 1.2 Hz, furyl), 7.40 (d, 1H, J = 3.6 Hz, furyl), 6.67–6.66 (m, 1H, furyl), 4.36 (q, 2H, J = 7.2Hz, CH_2), 1.38 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 157.5, 143.6, 143.2, 134.4, 116.7, 110.2, 108.8, 93.5, 57.5, 9.1.

Ethyl (E)-2-cyano-3-(3-pyridyl)-2-propenoate (Table 2, entry 16): Yellow solid; m.p. 76–78 °C(lit.[30]75–76 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.95 (d, 1H, J = 2 Hz, pyridyl), 8.76 (d, 1H, J = 7.2 Hz, pyridyl), 8.59–8.57 (m, 1H, pyridyl), 8.27 (s, 1H, C=CH), 4.41 (q, 2H, J = 7.2 Hz, CH_2), 1.42 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 161.6, 153.3, 152.8, 151.2, 135.8, 127.4, 123.9, 114.8, 105.5, 62.9, 14.0.

Ethyl (E)-2-cyano-3-phenyl-2-propenoate (Table 1, entry 3): White solid; m.p. 47–48 °C(lit.[28]47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.36 (s, 1H, C=CH), 8.00 (d, 2H, J = 7.6 Hz, ArH), 7.59–7.49 (m, 3H, ArH), 4.39 (q, 2H, J = 7.2 Hz, CH_2), 1.4 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm): 162.4, 155.0, 133.3, 131.4, 131.0, 129.2, 115.5, 102.9, 62.7, 14.1.

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References

1 L.F. Tietze, *Chem. Rev.*, 1996, **96**, 115.
2 L.F. Tietze and U. Beifuss, *Comprehensive organic synthesis*, eds B.M. Trost, I. Fleming, C.H. Heathcock, Pergamon Press, Oxford, 1991; Vol. 2, Chap.1.11, p. 341.
3 A.V. Narsaiah, A.K. Basak, B. Visali and K. Nagaiah, *Synth. Commun.*, 2004, **34**, 2893.
4 C. Mukhopadhyay and A. Datta, *Synth. Commun.*, 2008, **38**, 2103.
5 A. Sebti, A. Smahi and A. Solhy, *Tetrahedron Lett.*, 2002, **43**, 1813.
6 J.J. Han, Y.F. Xu, Y.P. Su, X.G. She and X.F. Pan, *Catal. Commun.*, 2008, **9**, 2077.
7 G. Cardillo, S. Fabbroni, L. Gentilucci, M. Gianotti and A. Tolomelli, *Synth. Commun.*, 2003, **33**, 1587.
8 D.S. Acker and W.R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370.
9 Y.M. Ren and C. Cai, *Synth. Commun.*, 2007, **37**, 2209.
10 W.B. Yi and C. Cai, *Catal. Commun.*, 2008, **9**, 1291.
11 W. Bao, Y. Zhang and J. Wang, *Synth. Commun.*, 1996, **26**, 3025.
12 P. Shanthan Rao and R.V. Venkatratnam, *Tetrahedron Lett.*, 1991, **32**, 5821.
13 O. Attansi, P. Fillippone and A. Mei, *Synth. Commun.*,1983, **13**, 1203.
14 A.V. Narsaiah and K. Nagaiah, *Synth. Commun.*, 2003, **33**, 3825.
15 B.M. Reddy, M.K. Patil, K.N. Rao and G.K. Reddy, *J. Mol. Catal. A: Chem.*, 2006, **258**, 302.
16 P. Leelavathi and S. Ramesh Kumur, *J. Mol. Catal. A: Chem.*, 2005, **240**, 99.
17 C. Paun, J. Barklie, P. Goodrich, H.Q.N. Gunaratne, A. Mckeown, V.I. Pârvulescu and C. Hardacre, *J. Mol. Catal. A: Chem.*, 2007, **269**, 64.
18 R.N. Ghosh, *Synlett*, 2004, 574.
19 V.K. Aggarwal, *Chem. Commun.*, 1999, 2311.
20 C.E. Yeom, M.J. Kim and B.M. Kim, *Tetrahedron*, 2007, **63**, 904.
21 G.K. Kakade, B.R. Madje, R.U. Pokalwar, M.N. Ware and M.S. Shingare, *Indian J. Het. Chem.*, 2008, **17**, 379.
22 W.W. Miao and T.H. Chan, *Acc. Chem. Res.*, 2006, **39**, 897.
23 A.G. Ying, X.Z. Chen, W.D. Ye, D.F. Zhang, L. Liu and J.H. Chen, *Prog. Chem.*, 2008, **20**, 1642.
24 A.G. Ying, W.D. Ye, L. Liu, G.F. Wu, X.Z. Chen, S. Qian and Q.P. Zhang, *Chin. J. Org. Chem.*, 2008, **28**, 2081.
25 A.G. Ying, L. Liu, G.F. Wu, G. Chen, X.Z. Chen and W.D. Ye, *Tetrahedron Lett.*, 2009, **50**, 1653.
26 M.L. Deb and P.J. Bhuyan, *Tetrahedron Lett.*, 2005, **46**, 6453.
27 J.C. Zhang, T. Jiang, B.X. Han, A.L. Zhu and X.M. Ma, *Synth. Comuun.*, 2006, **36**, 3305.
28 Y. Hu, J. Chen, C.G. Le and Q.G. Zheng, *Synth. Commun.*, 2005, **35**, 739.
29 C.B. Yue, A.Q. Mao, Y.Y. Wei and M.J. Lǔ, *Catal. Commun.*, 2008, **9**, 1571.
30 W.B. Yi and C. Cai, *Catal. Commun*., 2008, **9**, 1291.
31 L.C. Rong, X.Y. Li, H.Y. Wang, D.Q. Shi, S.J. Tu and Q.Y. Zhuang, *Synth. Commun.*, 2006, **36**, 2407.
32 K.P. Boegesoe, *J. Med. Chem.*. 1983, **26**, 935.
33 S. Wang, Z. Ren, W. Cao and W. Tong, *Synth. Commun.*, 2001, **31**, 673.
34 X.S. Wang, Z.S. Zeng, Y.L. Li, D.Q. Shi, S.J. Tu, X.Y. Wei and Z.M. Zong, *Synth. Commun.*, 2005, **35**, 1915.
35 J.S. Yadav, B.V.S. Reddy, A.K. Basak, B. Visali, A.V. Narsaiah and K. Nagaiah, *Eur. J. Org. Chem.*, 2004, 546.