



## Original Research Article

# Water extract of onion catalyzed Knoevenagel condensation reaction: an efficient green procedure for synthesis of $\alpha$ -cyanoacrylonitriles and $\alpha$ -cyanoacrylates

Prabakaran Kaliyan, Sivakumar Matam, Seenivasa Perumal Muthu\* 

Department of Chemistry, The Gandhigram Rural Institute-Deemed to be University, Gandhigram, Dindigul district, Tamilnadu-624 302, India

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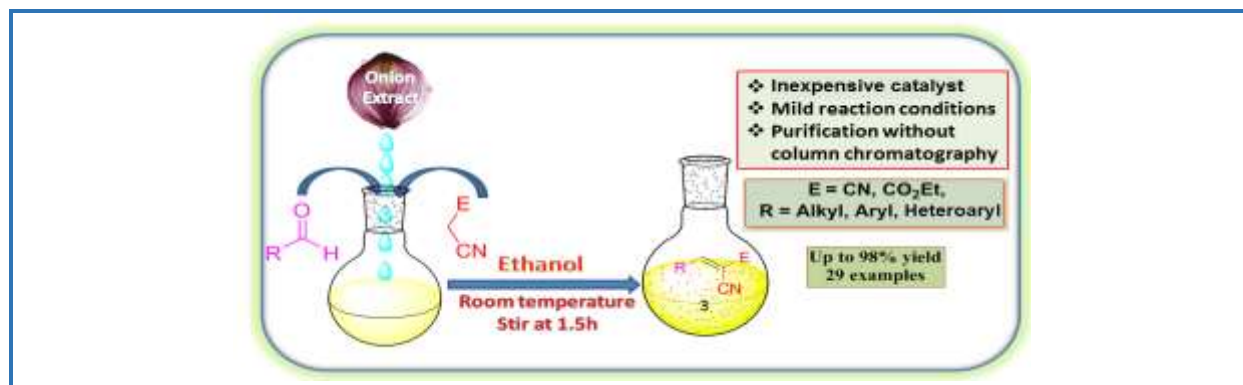
### KEYWORDS

Knoevenagel product  
Malononitrile  
Aldehydes  
Water extract of onion

### ABSTRACT

A useful method for Knoevenagel condensation has been developed from the reaction between active methylene compound **1** and aldehyde **2** using the water extract of onion as a green catalyst. This method is suitable for a variety of aldehydes; including, substituted aromatic, aliphatic,  $\alpha$ ,  $\beta$ -unsaturated as it heterocyclic with malononitrile or ethyl cyanoacetate, and affords the  $\alpha$ -cyanoacrylonitriles and  $\alpha$ -cyanoacrylates with excellent yields (Up to 98%). The products are isolated without column chromatography. The use of water extract of onion has several advantages such as low price, easy handling, simple work up and environmentally benign procedure.

## Graphical Abstract



## Introduction

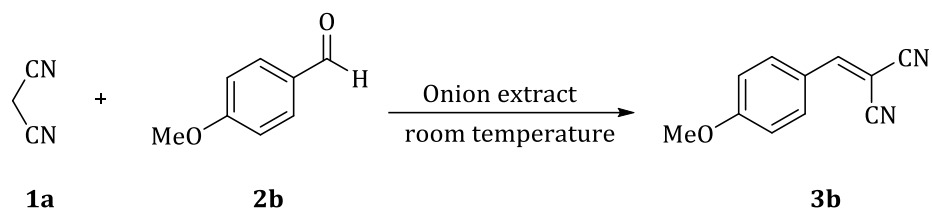
The Knoevenagel reaction has been widely used to construct a carbon-carbon double bond from an activated methylene compounds and substituted aldehydes [1–4]. The formed alkene products are highly useful intermediates for the synthesis of the organic molecules such as heterocyclic compounds [5–7], natural products, anti-hypertensive drug, coumarin derivatives, perfumes, and cosmetics [8–13]. It is typically performed in organic solvents in the presence of bases such as primary or secondary amines and their salts. Recently, a wide range of catalysts; including; Lewis acids [14–19], heterogeneous catalysts [20–34], ionic liquids [35–41], metal oxides [42–48], zeolites [49–51], polymer-supported amines [52–53], amino acids [54–56] and ionic exchange resins [57–58] have been used to catalyze this reaction. However, many of these methods have some limitations. Occasionally, the reaction needs expensive or toxic reagents, drastic condition, extensive reaction time. Moreover, it requires alteration of the reaction conditions, like microwave radiation [2–3, 12] or ultra-sonication [21, 36, 54, 57]. In several cases [59–62], the variety of aldehydes were limited to only aromatic aldehydes. In this sense, a very few examples have applied aliphatic aldehydes at room temperature with good yields.

$\alpha$ -Cyanoacrylates and acrylonitriles are an important class of compounds, and have a tendency to stick wide range of substrates, therefore they are highly useful in industry and for homeowners [63–66]. They were quickly polymerized without any additional agents and formed a strong bond between two adherends. Due to its biocompatibility, low toxicity and biodegrade ability, it gained many biomedical applications such as tissue adhesives [63–66], antibacterial [67], hemostatic [68], drug delivery [69], and fingerprint development in forensic sciences [70]. The co-polymer of 1,3-butadiene and acrylonitrile is called Buna-N rubber. Acrylonitriles were readily polymerized to form

linear polymers having fibrous characteristics. A small portion of acrylate added to the acrylonitrile, improves the dyeing characteristic [71].

Presently, in organic synthesis, the development of environmentally benign and economical processes are highly demandable. Keeping that in mind, a simple, a high yielding method for the preparation of  $\alpha$ -cyano acrylate and  $\alpha$ -cyanoacrylonitrile is being reported by Knoevenagel condensation between active methylene compounds with aliphatic, aromatic and heteroaromatic aldehydes in good to excellent yields using readily available, and inexpensive water extract of onion as a catalyst. The reaction was carried out using equimolar amounts of active methylene compounds with aldehydes in the presence of 2 mL of water extract of onion at room temperature to give Knoevenagel condensation product **3b** in excellent yield (Scheme 1). Under identical conditions and without water extract of onion, it gave the traces of the product, and thus the role of onion extract was highlighted. Number of organic reactions using various fruit juices are reported in the literature [72]. Due to their acidic nature, aqueous fruit juices such as lemon [73], pineapple [74], coconut [75], and tamarind [76] have been found to be useful in homogeneous acid catalysis.

The onion (*Allium Cepa* L.) is one of the most popular and commonly consumed vegetables. It is also a very good source of phytochemicals such as organo sulfur and flavonoid quercetin. The composition of the phytochemical may vary in accordance to geography, seasonal harvesting and processing. Due to the presence of these phytochemicals, it has many applications in material chemistry [77–78] (Nanoparticle preparation) and medicinal field; including, anticancer, anti-inflammatory, antiproliferative, reducing serum cholesterol, and blood pressure, immune stimulation, surgical scars, ability to modulate the detoxification system and free radical scavenging activity [79–87]. The main constituent of onion is 1-propenylcysteine sulfoxide (Isoalliin, an alkylated cysteine sulfoxide). When the onion is cut, the isoalliin undergoes a series of rapid reactions. The enzyme Alliinase catalyzes the conversion of 1-propenylcysteine sulfoxide to (E)-1-propenesulfenic acid, which is then rearranged to the volatile and highly reactive lachrymatory factor (LF) (Z)-propanethial S-oxide, [88–89] which produces acetaldehyde, sulphuric acid and hydrogen sulfide [90–91]. The prepared onion extract is an acidic in nature, having the pH of 3.6 with the strength of 0.0034 N. So, it may work as acid catalyst for condensation reactions (Scheme 1). Therefore, this water extract of onion has been employed as a catalyst for Knoevenagel condensation reaction. We report, herein, onion extract catalyzed Knoevenagel condensation reaction of active methylene compounds with various aldehydes such as aromatic, aliphatic, heterocyclic and  $\alpha$ ,  $\beta$ -unsaturated (Scheme 1).



**Scheme 1.** General scheme for the synthesis of  $\alpha$ -cyanoacrylonitriles and  $\alpha$ -cyanoacrylates

## Experimental

### Materials and methods

$^1\text{H}$  NMR (300 MHz or 400 MHz) and  $^{13}\text{C}$  NMR (75 MHz or 100 MHz) were recorded by BRUKER-FT NMR spectrometer using DMSO- $d_6$  or  $\text{CDCl}_3$  as a solvent and TMS as an internal standard (Chemical shift in  $\delta$  ppm). The chemical shifts are expressed in downfield from the signal of internal Tetramethylsilane (TMS). The infrared spectra were recorded on JASCO FT-IR spectrophotometer model 400 plus using dry KBr pellets. Melting points were determined using a Guna Enterprises, India capillary on melting point apparatus and are uncorrected. Analytical thin layer chromatographic tests were carried out on glass plates ( $3 \times 10$  cm) coated with 250  $\mu\text{m}$  Merck GF<sub>254</sub> silica gel. The spots were visualized by short exposure to iodine vapour or UV light. Ethyl-2-cyanoacetate and Malononitrile were purchased from CDH, India, and Spectrochem, PVT. LTD, India. Anisaldehyde, o-nitrobenzaldehyde, benzaldehyde, 4-chlorobenzaldehyde, cinnamaldehyde, crotonaldehyde were purchased from SRL, India. 4-cyanobenzaldehyde, 4-hydroxybenzaldehyde, 4-nitrobenzaldehyde, thiophene-2-carboxaldehyde, furfural, anthraldehyde, and 4-fluorobenzaldehyde were supplied by Sigma Aldrich, USA. The solvent ethanols were purchased from Changshu Yangquan chemicals, china and were further purified by dry distillation method.

### General procedure

To a stirred solution of active methylene compound **1** (2 mmol), aldehyde **2** (2 mmol) in ethanol (5 mL) was added onion extract (2 mL) at room temperature. After 15 min, pale yellow precipitate was observed. Further, the reaction mixture was stirred at this temperature for respective time given in the [Table 3](#). The progress of the reaction was monitored by TLC. After complete conversion of the starting material, the pale yellow solid was filtered, and, then, washed with chilled ethanol (5 mL) to afford the Knoevenagel condensation product **3** in good yield. The products are re-crystallized in ethanol.

### 2-(4-hydroxybenzylidene)malononitrile **3a**

Pale yellow solid, yield 0.285 g (84%), mp 186-188 °C (Lit [29], 187-189 °C), IR (KBr) ( $\nu_{\max}$ /  $\text{cm}^{-1}$ ): 3353, 3029, 2924, 2230, 1610, 1564, and 837  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  11.15 (s, 1H), 8.37 (s, 1H), 7.96 (d, J 8.8 Hz, 2H), 7.04 (d, J 8.4 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  164.3, 160.9, 134.3, 123.2, 117.0, 115.5, 114.6, 75.5.

### 2-(4-methoxybenzylidene)malononitrile **3b**

Yellow solid, yield 0.361 g (98%), mp 108-110 °C (lit [18], 119 °C), IR (KBr) ( $\nu_{\max}$ /  $\text{cm}^{-1}$ ): 3435, 3028, 2919, 2851, 2223, 1605, 1571, 1512, 1278, 1185, 1022, 834, and 571  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.37 (s, 1H), 7.96 (d, J 8.8 Hz, 2H), 7.17 (d, J 8.8 Hz, 2H), 3.86 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ):  $\delta$  164.8, 160.9, 133.8, 124.6, 115.6, 115.2, 114.3, 77.3, 56.3.

## Results and discussion

In continuation of our previous work [92] towards developing new methods using onion extract as catalyst, we have studied the reaction between the active methylene group **1** and aldehyde **2**. The reactions were proceeded smoothly in the presence of onion extract (2 mL) to afford the Knoevenagel product **3** in good to excellent yields (Up to 98%). The preparation process required water extract of onion as reported earlier from our research group [92]. Since, the prepared water extract of onion is pH 3.6, we have carried out the control experiments using HCl (pH 3.6),  $\text{H}_2\text{SO}_4$  (pH 3.6) in ethanol for 2 h. These acids also catalysed the reaction and gave lesser yield than onion extract catalyst. The optimization of the catalyst loadings is summarised in Table 1.

Further efforts were undertaken to optimize solvent. The results are summarized in Table 2. We have chosen polar solvent such as  $\text{H}_2\text{O}$ , methanol, ethanol, 2-PrOH,  $\text{CH}_2\text{Cl}_2$ , MeCN, DMF, DMSO, hexane, and AcOH solvent for our study.

After optimizing the reaction condition, we have examined the scopes and limitations of the onion extract catalyst, various active methylene compounds such as malononitrile (pKa=8) [93] **1a**, ethyl cyanoacetate (pKa=9) [93] **1b**, diethyl malonate (pKa=13.3) [93] **1c**, ethyl acetoacetate (pKa=10.7) [93] **1d**, acetonyl acetone (pKa=14.15) [94] **1e**, benzoyl acetone (pKa=14.25) [94] **1f** and benzoyl methane (pKa=15.2) [94] **1g** were treated with a range of aliphatic, aromatic, heterocyclic and  $\alpha$ ,  $\beta$ -unsaturated aldehydes in the presence of catalytic amount of onion extract in ethanol. The results are summarised in Table 3. The reaction was clean and proceeded smoothly to give corresponding Knoevenagel product in good to excellent yields.

The appearance of olefinic proton at  $\delta$  7.48 to 8.34 which indicated the products **3o-3ac** was only *E* geometry [**1c-d**, **6b**, **6g**] [95-98]. The nucleophilic addition of active methylene groups to aldehydes, catalysed by onion extract was found to be dependent on electronic factors of the active

**Table 1.** Optimization of study for catalyst quantity<sup>a</sup>

Entry	Onion extract (mL)	Time (h)	Yield (%)
1	0.1	2	57
2	0.4	4	67
3	0.5	4	80
4	1.0	3	88
5	1.5	3	93
6	2.0	2.5	98
7	0	3	Trace

<sup>a</sup> Model reaction: malononitrile **1a** (1 eq) and anisaldehyde **2b** (1 eq) in the presence of onion extract with different concentrations and time in 5 mL of EtOH

**Table 2.** Optimization of reaction condition with various solvents<sup>a</sup>

Entry	Solvents	Yield (%)
1	H <sub>2</sub> O	70
2	MeOH	89
3	EtOH	98
4	2-PrOH	76
5	CH <sub>2</sub> Cl <sub>2</sub>	59
6	MeCN	77
7	DMF	74
8	DMSO	78
9	Hexane	74
10 <sup>b</sup>	AcOH	71

<sup>a</sup> Model reaction: malononitrile **1a** (1 eq) and anisaldehyde **2b** (1 eq) with various solvents (5 mL) in the presence of onion extract (2 mL) at room temperature for 2.5 h

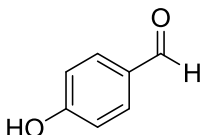
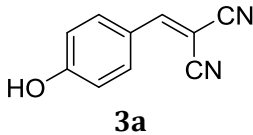
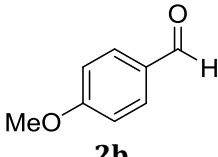
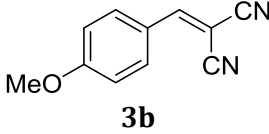
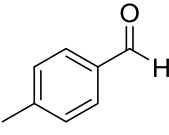
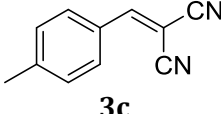
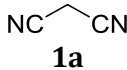
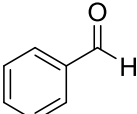
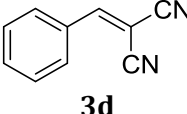
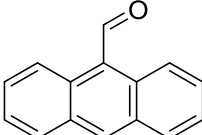
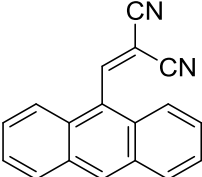
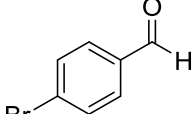
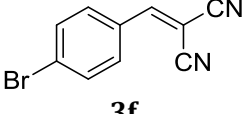
<sup>c</sup> The reaction was carried out using anisaldehyde **2b** (1 eq), malononitrile **1a** (1 eq) in AcOH (5 mL) at room temperature for 6 h

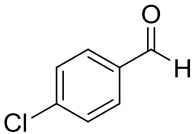
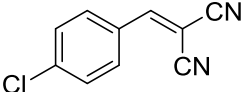
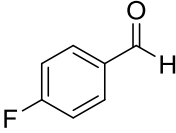
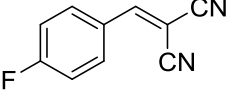
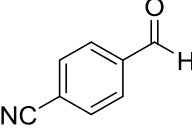
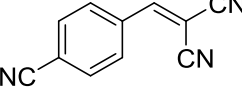
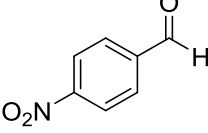
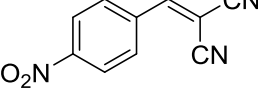
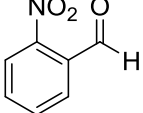
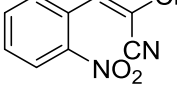
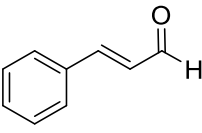
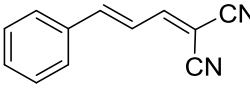
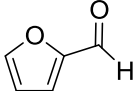
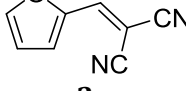
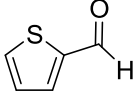
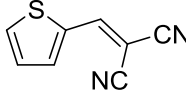
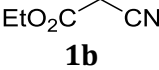
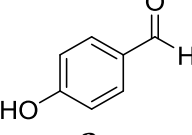
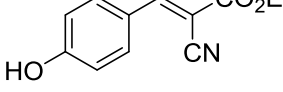
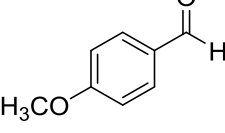
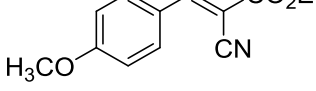
methylene compounds and the aldehydes. The different reactivities of the active methylene compounds were found to be depended on the different pKa values. The malononitrile (pKa=8) [93] **1a**, requires lesser period than ethyl cyanoacetate **1b**, (pKa=9) [93] to complete the reaction. This may be due to the acidity of the active methylene compounds. In the case of active methylene compounds **1c-1g** (pKa=10.7-15.2), no reaction was observed even after the extended heating (24 h) at reflux temperature. It was concluded that, as the pKa value increased, the reactivity of the active

methylene compounds reduced. The pKa of active methylene compound >9 the reaction does not proceeded.

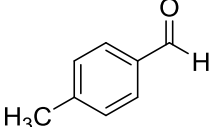
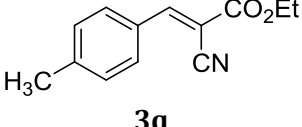
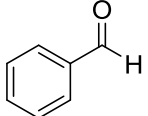
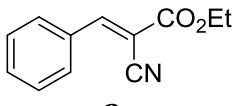
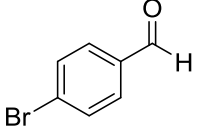
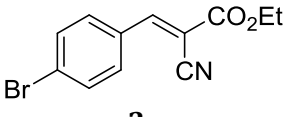
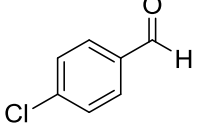
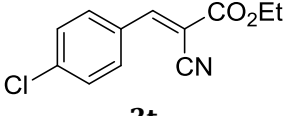
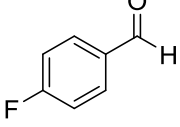
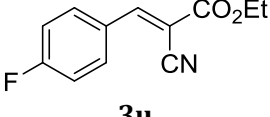
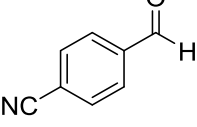
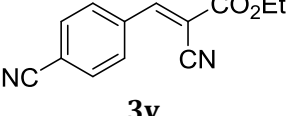
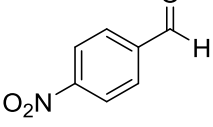
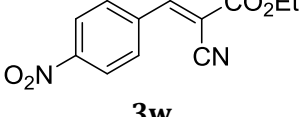
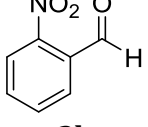
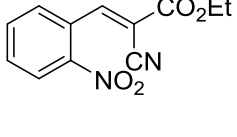
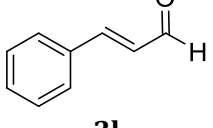
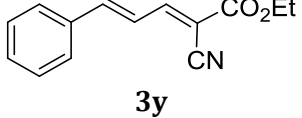
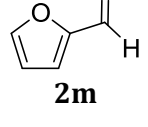
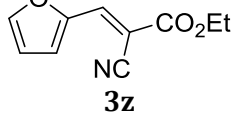
The different reactivities of the aldehydes were dependent on the substituents on the benzene ring. The presence of electron withdrawing group on the benzene ring increased the reactivity of the substance (Table 3, entry 6-11 and 19-24). An electron-releasing substituents presented on the benzene ring were observed with a relatively lesser yield than the electron-withdrawing substituents (Table 3, entry 1-3 and 15-17). No significant effect was observed on o-substituted aldehydes (Table 3, entry 11 and 24). Furthermore, we have examined the reaction between malononitrile **1a** and ketones such as cyclohexanone and acetone. Unfortunately, the corresponding Knoevenagel products were not produced under these conditions. Since water extract of onion available plenty, cheap and natural. Hence, we could not try anything regarding recyclability of the catalyst.

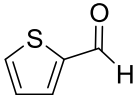
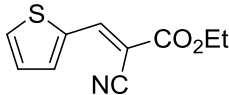
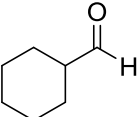
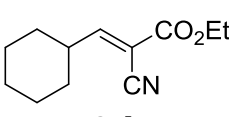
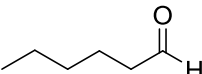
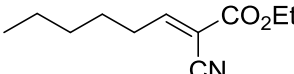
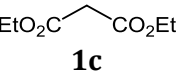
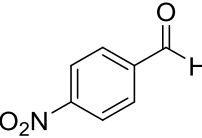
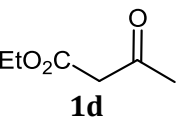
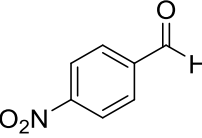
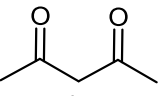
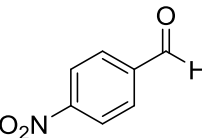
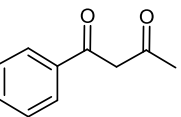
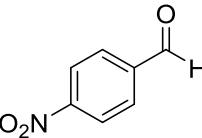
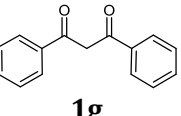
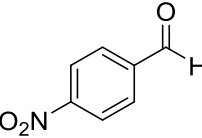
**Table 3.** Synthesis of Knoevenagel product<sup>a</sup> **3**

Entry	E 1	R 2	Product 3	Time (h)	Yield (%)
1				2.5	84
2				2.5	98
3				2.5	81
4				3.5	80
5				2.5	93
6				2	94

7	 <b>2f</b>	 <b>3g</b>	2	90	
8	 <b>2h</b>	 <b>3h</b>	1.5	96	
9	 <b>2i</b>	 <b>3i</b>	1.5	93	
10	 <b>2j</b>	 <b>3j</b>	1.5	96	
11	 <b>2k</b>	 <b>3k</b>	1.5	95	
12	 <b>2l</b>	 <b>3l</b>	3.5	69	
13	 <b>2m</b>	 <b>3m</b>	1.5	98	
14	 <b>2n</b>	 <b>3n</b>	2	87	
15	 <b>1b</b>	 <b>2a</b>	 <b>3o</b>	8	85
16	 <b>2b</b>	 <b>3p</b>	4	76	



17	 <b>2c</b>	 <b>3q</b>	4	61
18	 <b>2d</b>	 <b>3r</b>	7.5	85
19	 <b>2f</b>	 <b>3s</b>	7	83
20	 <b>2g</b>	 <b>3t</b>	7	79
21	 <b>2h</b>	 <b>3u</b>	2.5	91
22	 <b>2i</b>	 <b>3v</b>	2.5	94
23	 <b>2j</b>	 <b>3w</b>	2.5	97
24	 <b>2k</b>	 <b>3x</b>	3	89
25	 <b>2l</b>	 <b>3y</b>	6	81
26	 <b>2m</b>	 <b>3z</b>	4	89

27			4	84
28			6	90
29			4	93
30 <sup>b</sup>			-	24
31 <sup>b</sup>			-	24
32 <sup>b</sup>			-	24
33 <sup>b</sup>			-	24
34 <sup>b</sup>			-	24

<sup>a</sup>All the reactions were carried out by using aldehyde **2** (2 mmol) and active methylene **1** (2 mmol) in ethanol (5 mL) at room temperature in the presence of onion extract (2 mL) for specific period mentioned in the [Table 3](#)

<sup>d</sup>All the reaction was carried out by using 4-NO<sub>2</sub>-benzaldehyde **2j** (2 mmol) and malononitrile **1a** (2 mmol) in ethanol (5 mL) at reflux in the presence of onion extract (2 mL) for 24 h

To evaluate the possibility of applying this methodology in a large scale synthesis, we have carried out the reaction of equimolar amounts of (50 mmol) malononitrile **1a** with 4-nitrobenzaldehyde **2j**. The Knoevenagel product **3j** was obtained in 97% yield. Previously, it was reported in the literature that the pineapple juice [74] (pH 3.7) and onion extract (pH 3.6 reported by us) have been employed as catalysts for Knoevenagel condensation and enaminone synthesis [92] respectively. Accordingly, a plausible mechanism has been proposed (Figure 1).

Table 4 compares the catalytic activity of onion extract catalyst with the recently reported catalytic system in the Knoevenagel condensation reaction. Although less quantity of the catalyst was used (Table 4, entries 1-4), it required more time or high temperature and even gave less yield than present study. When fruit juices were used as catalysts (Table 4, entries 5 and 6) for Knoevenagel condensation with a lesser amount of the catalyst and reduced time, the yields are slightly lesser than present study. Hence, onion extract catalyzed Knoevenagel condensation is superior over other reported methods.

## Conclusion

We have achieved a simple and convenient procedure to synthesize the  $\alpha$ -cyanoacrylonitriles and  $\alpha$ -cyanoacrylates through Knoevenagel condensation from the easily available aldehydes and active methylene compounds. In this process, water extract of onion is used as a green catalyst. The products are precipitated as yellow solid, do not require any further purification and obtained only the *E*-isomers. Also, we have demonstrated this methodology for large scale synthesis where we used equimolar quantities of substrates. Though these reactions are catalyzed by HCl and H<sub>2</sub>SO<sub>4</sub>, the water extract of onion catalyzed reactions has some advantages; including, being environmentally friendly, easy availability, low cost, easy handling, and simple workup procedure.

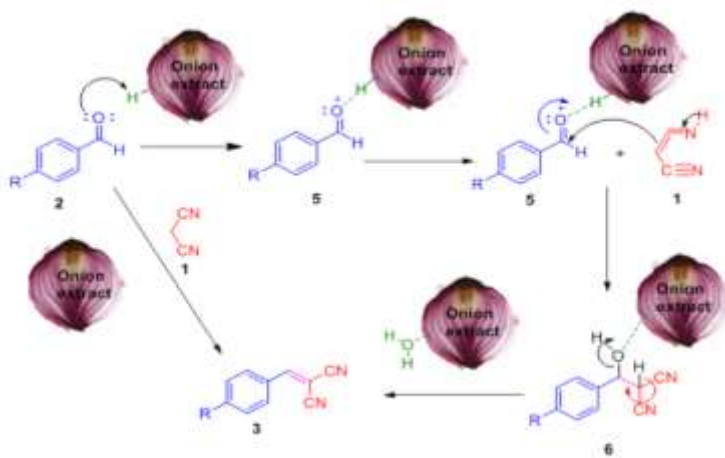


Figure 1. Proposed mechanism

**Table 4.** Recently reported green catalytic system

Entry	Catalyst	Reaction time	Yield (%)	Ref
1	Graphene oxide	0.5 mL of catalyst (1.5 mg/mL), RT, 4 h,	83	22
2	Silica Supported Ammonium Acetate	0.2 g of catalyst in CH <sub>2</sub> Cl <sub>2</sub> , reflux, 7 h.	87	29
3	TPP	20 mol % of catalyst, 75-80 °C, 4 h	83	97
4	Lipase	200 mg of catalyst in DMSO, 35 °C, 24 h	98	11
5	Lemon juice	1 mL of catalyst, RT, 2 h	90	73
6	Pineapple juice	1 mL of catalyst, RT, 2 h	95	74
7	Water onion extract	2 mL of catalyst, RT, 2.5 h	98	-

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### Disclosure statement

No potential conflict of interest was reported by the authors.

### Orcid

Muthu Seenivasa Perumal  0000-0002-2234-1346

### Supporting Information

Additional supporting information related to this article can be found, in the online version, at DOI:[10.22034/ajgc.2018.137885.1079](https://doi.org/10.22034/ajgc.2018.137885.1079)

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