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# DBU: A Smart Organo Catalyst for The Green Synthesis Of 2-Cyano-3-Phenylacrylic Acid Derivatives at Room Temperature

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## Abstract

The synthesis of 2-cyano-3-phenylacrylic acid derivatives have been described by using aromatic aldehydes and ethyl cyanoacetate in water using acetamidine as a promoter in presence DBU as a organo catalyst. The reaction completed up to 30 minutes of time using DBU in water at an ambient temperature renders the protocol environment friendly. All the synthesized compounds have been confirmed on the basis of their IR, NMR and C<sup>13</sup> NMR.

**Keywords** 2-cyano-3-phenylacrylic acids, aromatic aldehydes, ethylcyanoacetate, DBU, water.

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## 1. Introduction

The conventional multistep synthesis of a complex molecule frequently involves a large number of synthetic operations, including extraction and purification processes in each individual step. This leads to not only synthetic inefficiency but also generates large amounts of wastes. Green chemistry robustly influences chemical research, and there is persistence on the use of greener reaction conditions [1]. Uses of volatile organic solvents are major contributors to environmental pollution [2]. In order to remove volatile organic solvents from the chemical process, significant aspect of green chemistry relates to the elimination of volatile organic solvents or use of non-flammable, non-volatile, non-toxic and inexpensive green solvents [3]. In this regard, use of green solvent is the most excellent way to minimize the environmental pollution.

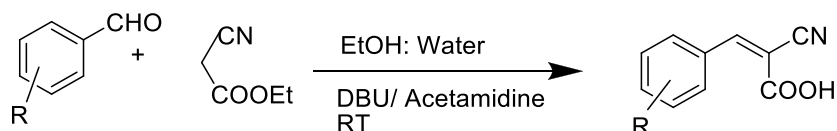
In recent years there is an enhanced public hopes that chemists and chemical

engineers should produce greener and more sustainable chemical processes. Various nonconventional reaction media have been intensively studied in recent years, including water [4], supercritical CO<sub>2</sub> [5-7] and ionic liquids [8-10] or in liquid-liquid biphasic combinations. As a reaction medium, water obeys with all the current severe requirements on sustainable chemistry. Therefore, the development of synthetically useful reactions in water is of considerable interest. It should be noted that a large list of examples in the recent chemical literature shows that organic reactions performed in water are not only typically faster but also display new reactivity profiles and selectivity. Water has many benefits: it is nontoxic, nonflammable, abundantly available, and inexpensive. Furthermore, performing the reaction in an aqueous biphasic system [11-12], whereby the catalyst resides in the water phase and the product is dissolved in the organic phase,

allows for recovery and recycling of the catalyst by simple phase separation.

Having in mind the importance of green solvents, herein we report an efficient method for synthesis of 2-cyano-3-

phenylacrylic acid derivatives using aromatic aldehydes and ethyl cyanoacetate in water using acetamidine as a promoter in presence DBU as a catalyst (**Scheme 1**).

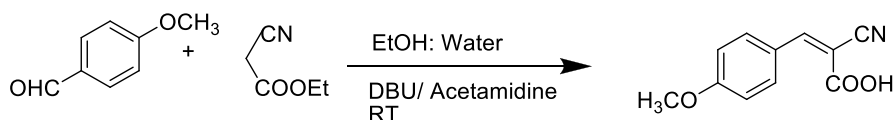


**Scheme 1:** General reaction for the synthesis of 2-cyano-3-phenylacrylic acid derivatives

## 2. Results And Discussion:

In the present protocol, we initiated our studies by employing a trial reaction of 4-methoxybenzaldehyde (1mmol) and ethylcyanoacetate (1mmol) in 5 ml ethanol-water mixture in presence of catalytic amount DBU was stirred at room temperature. It was found that desired product was not formed

after a longer time of reaction. When the said reaction was carried out by adding acetamidine hydrochloride and kept at room temperature for stirring up to completion monitored by TLC, the reaction mixture was poured on ice cold water and neutralized by few drops of dil. HCl. The desired product was obtained in excellent yield within half hour (**Scheme 2**).



**Scheme 2:** Synthesis of 2-cyano-3-(4-methoxyphenyl) acrylic acid

The said reaction was also carried out at room temperature using diethyl amine, piperidine and DBN, the desired product was obtained in 70%, 75 and 85% respectively.

Therefore, considering the effective catalytic activity of DBU, DBU is preferred as a catalyst for subsequent optimization studies. Varying the amount of DBU, it was found that 10 mol% of DBU was sufficient to get the most excellent results. (**Table 1**)

**Table 1: Screening and optimization of catalyst**

Sr. No	Catalyst	Catalyst conc. (mol %)	Yield (%)
1	Diethyl amine	10	70
2	Piperidine	10	75
3	DBN	10	85
4	DBU	10	95
5	DBU	15	96

The obtained product was isolated by simple filtration, washed with cold water and dried in an oven and confirmed on the basis of spectroscopic techniques. In IR spectrum of 2-cyano-3-(4-methoxyphenyl) acrylic acid a

sharp peak at  $2220\text{ cm}^{-1}$  was due to the  $-\text{CN}$  stretching. In  $^1\text{H-NMR}$  shows a sharp peak at  $\delta$  3.87 ppm which is due to the proton of methoxy group of aldehyde moiety and two doublet at  $\delta$  7.14-7.16 and 8.06-8.08 ppm are due aromatic protons. Single peak at 8.26 ppm

is due to the benzylic -CH- proton. The broad peak appeared at  $\delta$  13.80 ppm correspond to -COOH group. The  $^{13}\text{C}$ -NMR spectrum of said compound exhibit peak at 55, 99, 114, 116, 124, 133, 153, 163. The absence of peak of methyl group of acetamide in  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR support the formation of desired product and role of acetamide hydrochloride as a promoter. All the synthesized compounds have been confirmed on the basis of their spectroscopic data. The obtained data is in good agreement with the proposed structures.

In order to expand the scope of the present protocol, we have screened the various aldehydes bearing electron donating or electron withdrawing group gave an excellent yields. It has been observed that aldehydes bearing electron donating or electron withdrawing group did not affect the yield and reaction time of proposed method. All the result were presented in **Table 2**

**Table 2: Synthesis of 2-cyano-3-phenylacrylic acid derivatives \***

Entry	R	Time (Min)	Yield (%)
1	4-NO <sub>2</sub>	35	94
2	4-OCH <sub>3</sub>	40	95
3	3-OCH <sub>3</sub>	34	96
4	3,5-(OCH <sub>3</sub> ) <sub>2</sub>	34	94
5	4-Cl	35	93
6	3-Cl	32	93
7	Thiophen-2-yl	33	95
8	-N(CH <sub>3</sub> ) <sub>2</sub>	37	94

**\*Reaction Conditions:** Aldehydes (1 mmol), ethylcyanoacetate (1 mmol), acetamide hydrochloride, Solvent (5 ml) and catalyst (10 mol %).

### 3. General Procedure

A mixture of aromatic aldehydes (1 mmol), ethyl cyanoacetate (1 mmol), acetamide (1 mmol) and DBU (10 mol %) in mixture 3ml water and 2 ml ethanol was stirred at room temperature. After completion of reaction monitored by TLC, the reaction mixture was poured on ice cold water and neutralized by dil. HCl, a precipitate was collected by filtration and washed with cold water. The isolated obtained products were present in pure form and not require any further purification.

### 4. Conclusion

In the present study, the 2-cyano-3-phenylacrylic acid derivatives were prepared by a simple reaction of diverse aldehydes with ethyl cyanoacetate at room temperature. Easily available starting material, easy workup, mild reaction conditions and no need

of further purification of the product are advantages of said new protocol.

### 5. Spectroscopic Data Of Some Synthesized Representative Compounds.

#### 1. 2-cyano-3-(3-methoxyphenyl) acrylic acid

Yellow solid, Mp: 176-178 °C, yield: 96%; IR: 792, 1204, 1290, 1423, 1594, 1698, 2224 cm<sup>-1</sup>.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 3.73 (s, 3H, -OCH<sub>3</sub>), 7.20-7.22 (d, 1H, Ar-H), 7.48-7.52 (t, 1H, Ar-H), 7.62-7.63(d, 2H, Ar-H), 8.32 (s, 1H, -CH-), 14.03(br.s, 1H, -COOH);  $^{13}\text{C}$  NMR (75MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 55, 104, 115, 119, 123, 130, 159, 163.

#### 2. 2-cyano-3-(3, 5-dimethoxyphenyl) acrylic acid

Yellow solid, Mp: 180-182 °C, yield: 94%; IR: 736, 943, 1217, 1282, 1579, 1675, 2224 cm<sup>-1</sup>.  $^1\text{H}$  NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 3.80



(s, 3H, -OCH<sub>3</sub>), 3.87 (s, 3H, -OCH<sub>3</sub>), 7.17-7.19 (d, 1H, Ar-H), 7.69-7.71 (d, 1H, Ar-H), 7.78 (s, 1H, Ar-H), 8.35 (s, 1H, -CH-), 13.75 (br.s, 1H, -COOH); <sup>13</sup>C NMR (75MHz, DMSO-d<sub>6</sub>) δ (ppm): 55, 56, 111, 112, 124, 126, 149, 153, 154, 163.

### 3. 2-cyano-3-(thiophen-2-yl) acrylic acid

Brown solid, Mp: 212-214 °C, yield: 95%; IR: 764, 803, 1015, 1272, 1426, 1596, 2227. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ (ppm): 7.33-7.35 (t, 1H, Ar-H), 8.01-8.02 (d, 1H, Ar-H), 8.17-8.18 (d, 1H, Ar-H), 8.65 (s, 1H, -CH-), 13.78 (br.s, 1H, -COOH); <sup>13</sup>C NMR (75MHz,

DMSO-d<sub>6</sub>) δ (ppm): 93, 111, 117, 133, 153, 164.

### 4. 2-cyano-3-(dimethylamino phenyl) acrylic acid

Brown solid, Mp: 190-192 °C, yield: 94%; IR: 810, 1020, 1280, 1436, 1592, 2223. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ (ppm): 3.03 (s, 6H, -(NCH<sub>3</sub>)<sub>2</sub>), 6.82-6.84(d, 2H, Ar-H), 7.93-7.95 (d, 2H, Ar-H), 8.07 (s, 1H, -CH-), 13.29 (br.s, 1H, -COOH); <sup>13</sup>C NMR (75MHz, DMSO-d<sub>6</sub>) δ (ppm): 39, 111, 117, 118, 133, 153, 164.

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