

WEB: A green and an efficient catalyst for Knoevenagel condensation under grindstone method

K Kantharaju*, Prashant B Hiremath & S Y Khatavi

Department of Chemistry, Peptide and Medicinal Chemistry Research Laboratory,
Rani Channamma University, P-B, NH-4, Belagavi 591 156, India
E-mail: kk@rcub.ac.in

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A greener, economic and efficient approach for Knoevenagel condensation of substituted aromatic as well as heteroaromatic aldehydes with malononitrile catalyzed by water extract of banana (WEB) under grindstone method at room temperature is described. The total process is advantageous over conventional methods that involve reflux, heating and expensive approaches and also the reaction time is reduced. It is found that the reaction is clean with the separation of the solid product during grinding process and reaction can be carried out without use of organic solvent as well as expensive catalyst. The final product is isolated by simple filtration and characterized by several spectroscopic methods for the confirmation of the products.

Keywords: Green catalyst, Knoevenagel condensation, aldehyde, malononitrile, water extract of banana, grindstone method

The C-C bond forming reaction is studied widely and applied in many industrial process applications. One such important reaction is Knoevenagel condensation^{1,2}. It involves a dehydration step where aldehyde and active methylene reagent such as malononitrile condense to produce alkenes, which is electron deficient and used as a starting reagent for the coumarin synthesis, which find wide applications in organic synthesis including therapeutic drugs, perfumes, cosmetics, herbicides, insecticides, polymers and more³. In general, Knoevenagel condensation is carried out between carbonyl of aldehyde compounds and active methylene carbon catalyzed by a Lewis acid or base. In the past few decades vast number of catalysts have been reported, such as Al₂O₃⁴, CdI₂⁵, I₂-K₂CO₃⁶, K₃PO₄⁷, ZnCl₂⁸, KF-Al₂O₃⁹, CTMAB¹⁰, AlPO₄-Al₂O₃¹¹, K₁₀-ZnCl₂¹², Zn(OAc)₂¹³, silica gel¹⁴, xonothite¹⁵, diammonium hydrogen phosphate¹⁶, USY-Zeolites¹⁷, functionalized silica gel¹⁸, MCM-41 functionalized¹⁹, functionalised ionic liquid²⁰, ionic liquid functionalised SBA-15²¹, basic-ionic liquid²², microporous poly urethane²³, natural catalyst²⁴ and other catalysts have been reported²⁵⁻³⁰. In spite of the potential efficiency of these reported catalysts, some of these catalysts are limited by lower yields, longer reaction time, elevated temperature, high cost and requirement of toxic

solvents for the reaction. Thus, there is still a demand for novel methods which are greener, inexpensive, provide cleaner reaction, good yields and have simple work-up processes for the isolation. Nowadays, chemists are more concerned about environmental hazards of chemical reactions, which are also the cause of climate change and global warming. Pollution and environmental factors are the driving force behind today's requirement for eco-friendly catalysts. Dr Paul Anastas, in the early 1990's demonstrated the concept of sustainable chemistry and derived green chemistry³¹ as chemistry able to promote chemical technologies that minimize the liberation of hazardous substances in the design, production and use of chemical products. Since then, green chemistry has slowly come to be recognized as both methodology and culture for achieving sustainability. The use of organic solvents is objectionable in green chemistry, since they are one of the major sources for emissions of hazardous volatile organic compounds in the chemical industry. Organic solvents usage has been controlled with strong environmental legislation and many of the traditional solvents used in organic synthesis have been blacklisted by international regulations. In green chemistry, the solvent should be non-toxic, not inflammable or not hazardous or corrosive and should

not harm the environment. The need for eco-friendly solvents has provided the stimulus for the fine chemicals and pharmaceuticals industries to search for alternative solvents. The second generation green solvents such as ionic liquid³², water and supercritical fluids emerged to fulfil this expectation. In other industrial sectors also, water represents an excellent universal solvent with regard to cost, safety, availability, environmental concern, non-flammability and non-toxicity. For a long time water as reaction medium remained unexplored except for hydrolysis reactions, due to the belief that organic reagents require an organic solvent for reaction. Therefore, with most organic compounds being insoluble in water, water is not believed to be favourable towards organic reactions. Breslow and his team pioneered studies on Diels-Alder reactions³³ in aqueous medium in the early 1980's. Thereafter, there was increased recognition of the fact that organic reactions can proceed quite well in aqueous medium and offer quite a few advantages over use of conventional solvents. Nowadays, there are a large number of literature reports, wherein organic reactions have been carried out with water as a solvent³⁴. Some important examples are Claisen rearrangement³⁵, Sharpless reaction³⁶, aldol reactions^{37,38}, allylation reactions³⁹⁻⁴¹ and hydroformylation⁴².

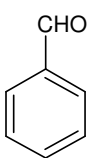
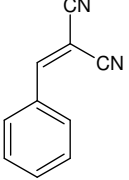
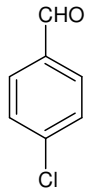
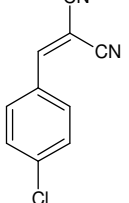
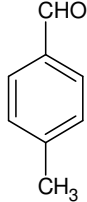
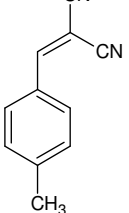
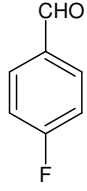
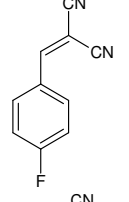
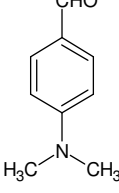
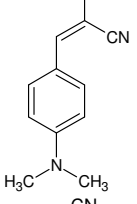
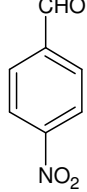
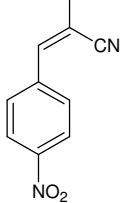
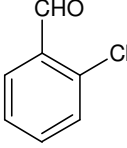
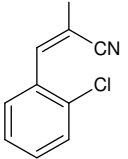
In this paper, we will introduce the extension of water extract media from agro waste material ash as a next-generation green catalyst for organic reactions, for sake of simplicity, greener method. It does not require expensive catalyst with the simple isolation of product after reaction with no further requirement of chromatographic purification. In principle, green chemistry aims to minimize the chemical waste. We selected agro waste stuff ash extract as a natural catalyst for the Knoevenagel condensation. It significantly fulfils our desired expectation of safe reaction strategy. We adopted the reported water extract of banana (WEB) extract procedure of Sarma *et al.*, but in this work, we selected locally available banana peel extract (*Musa acuminata*). Traditionally, some of the ash is used as detergents (papaya bark). Considering this property, it can be an alternative moderate base. In literature, only a limited number of methods are available, which significantly deal with water extract of burned ash of banana peels, papaya bark and rice straw employed as eco-friendly catalytic systems. These ash extract media have been well explored in some of the organic reactions such as

Suzuki-Miyaura cross-coupling reaction⁴³, Sonogashira coupling⁴⁴, peptide bond formation⁴⁵, coumarin synthesis⁴⁶ and several others. In the literature, it has been well studied and reported that burnt ash agro-waste generally contains K, Na, CO₃²⁻ and Cl⁻ as major constituents along with a host of other trace elements like Cu, Mg, Ca. It is believed that carbonates of Na and K of burnt ash extract³⁵ act as bases and other salts and counter ion act as promoters for the organic reaction. The pH of burnt ash extract of banana peels has been checked and it was found to exhibit pH of 11.94. The highly basic nature of the extract plays an important role in the condensation of an aldehyde with malononitrile which has resulted in the isolation of Knoevenagel product in pure form (Table I).

Results and Discussion

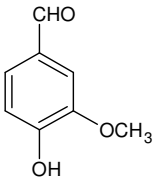
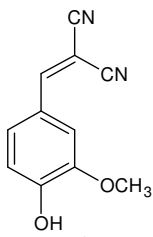
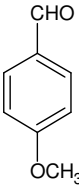
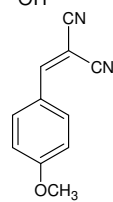
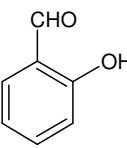
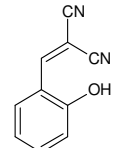
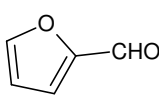
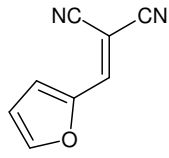
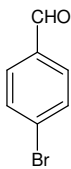
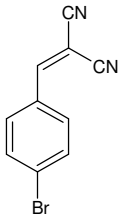
Considering recent environmental hazards, researchers are striving to establish novel eco-friendly reaction concepts by employing agro-waste stuff ash extract as a next-generation catalytic media for green method synthesis of organic molecules. These extracted solutions will provide the alternative green method. In addition, this will also replace chemicals and act as a natural basic media as an added advantage. Here, we adopted the procedure reported by Sharma *et al.*⁴⁵ for the extract of WEB, but in this work, we have selected locally available banana peels (*Musa acuminata*). The dried banana peels were burnt directly and resulted in 5 g of blackish powder. This was taken and suspended in 100 mL distilled water, stirred for 2 h at RT, filtered and the clear solution obtained is referred to as Water Extract of Banana (WEB). The composition of the extract was examined by author group by using EDX and flame photometry analysis. The report revealed a very high concentration of the oxides of Na⁺, K⁺, Mg⁺, *etc.* Since these metal oxides can react with water to produce metal hydroxides, it causes the solution to become basic. The same result is also confirmed by pH test that showed the extract solution having about pH 11.94. Reports in the literature describe the use of the base as a catalyst for Knoevenagel condensation, where active methylene proton abstraction takes place followed by nucleophilic substitution on carbonyl of aldehyde which resulted in an electron deficient olefin generation. This reaction has been extensively studied under various conditions, solvents and catalysts, and is commonly catalyzed by a Lewis acid or base.

Table I — Knoevenagel condensation of aromatic aldehydes with malononitrile (*Contd.*)

Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)	m.p. (°C)	
					Obsd	Lit.
1			6	93	83	84
2			5	89	164	163
3			7	88	164	166
4			8	85	124	127
5			4	87	180	182
6			6	89	158	157
7			7	85	77	79

(Contd.)

Table I — Knoevenagel condensation of aromatic aldehydes with malononitrile (*Contd.*)

Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)	m.p. (°C)	
					Obsd	Lit.
8			6	90	134	135
9			8	88	117	115
10			7	81	157	158
11			9	80	71	72
12			10	84	157	155

^a All the products were characterized by FT-IR, ¹H and ¹³C NMR, HR-MS and the observed m.p. are comparable with the reported literature data.

^b Yields refer to the isolated yields.

Here, we report Knoevenagel reaction of substituted aromatic aldehydes with malononitrile which resulted in aldol reaction followed by dehydration in one pot using mechanochemical grinding method (Figure 1) catalyzed by WEB. To our knowledge, this is the first reported method that employed agro-waste stuff ash extract catalyzed Knoevenagel condensation by grinding method at RT in the absence of a solvent. The previously reported catalysts and solvents for the Knoevenagel condensation reaction under different conditions is tabulated in Table II. In Table II the added advantage of using WEB as a catalyst media for the Knoevenagel condensation reaction is clearly demonstrated. Knoevenagel reaction has been found to be very

simple and does not require stirring or elevated temperature, no solvent and it is an eco-friendly method for the isolation of solid within 4-10 min grinding in pestle and mortar at RT. The extension to various substituted aromatic aldehydes is examined with malononitrile and it is found that the reaction method is very much compatible with a variety of substituted aldehydes as well as heterocyclic aldehydes. In order to verify the role of grinding, we have examined the model reaction (entry 1) of benzaldehyde with malononitrile left standing in pestle and mortar at RT for 24 h. A negligible amount of product separation could be observed. The mixture was also stirred magnetically at RT but the separation of product observed after a longer time (1-2 h), which

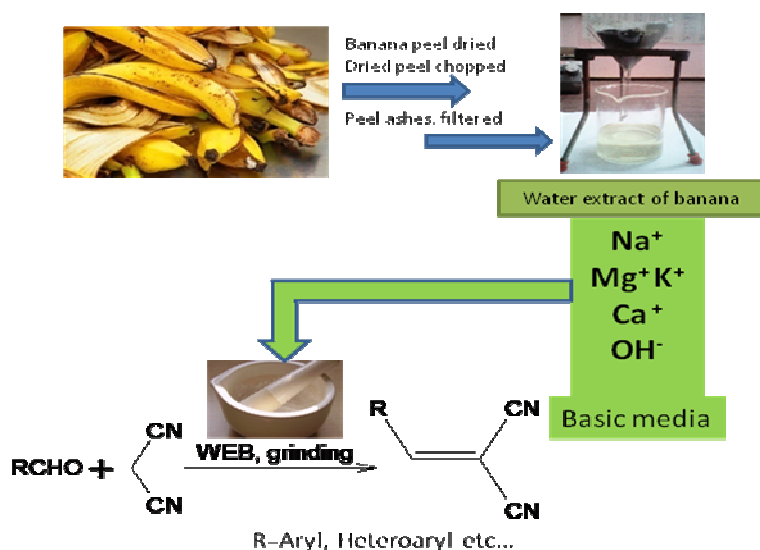


Figure 1 — WEB catalysed synthesis of Knoevenagel products

Table II — Comparison of different catalytic approaches used for the synthesis of 2-(Phenylmethylene)malononitrile

S.No	Catalyst	Solvent, Condition	Time	Yield (%)	Lit. Ref.
1	USY Zeolite	Benzene, reflux	12 h	92	17
2	SiO ₂ -NH ₄ OAc	DCM, stirred at 60°C	7 h	87	48
3	SO ₄ ⁻² ion promoted ZrO ₄	N ₂ atm, reflux	180 min	89	49
4	MOF-RNH ₂	Toluene, RT	2 h	99	50
5	MgBr ₂ .OEt ₂	TEA, THF, RT	1-2 h	98	51
6	CTMAB	Water, RT	1.5 h	90.6	10
7	Fe ₂ (SO ₄) ₃	DCM, RT	20 min	93	52
8	AlPO ₄ -Al ₂ O ₃	Neat, RT	15 min	80	11
9	H ₃ PW ₁₂ O ₄₀	Water, reflux	15 min	91	53
10	I ₂ /K ₂ CO ₃	EtOH/DMF, RT	12 min	80	6
11	GaCl ₃	Neat, grinding	2 min	98	54
12	WEB	Neat, grinding	6 min	94	This work

was more compare to grinding method. To keep this method economical, here we have used a china mortar and pestle under WEB catalysis. Similar grindstone method was also reported by Tong *et al.*⁴⁷, but they employed special a glass mortar and pestle for the Knoevenagel condensation reaction, and they reported that using china pestle and mortar was not successful for obtaining the Knoevenagel product. The exact mechanistic pathway by using WEB has not been shown, but we believe that it is an alternative to or replacement of the inorganic base by natural base (WEB) and there is scope for further research in this area. The advantages of this approach have also been studied by comparing it with other reported methods from the literature, as shown in Table II. However,

the Knoevenagel reaction carried out by grinding is free from the use of organic solvents, with less reaction time, does not require an expensive catalyst and follows a simple work-up procedure to provide a pure product upon isolation. All the synthesized products were structurally elucidated by using physical data and spectroscopic methods such as FT-IR, ¹H and ¹³C NMR, mass spectrometry and compared with literature data.

Materials and Methods

Laboratory grade chemicals were purchased from commercial sources and used as received without further purification. Melting points were determined in open capillaries and are uncorrected. FT-IR spectra

were recorded in KBr pellets on a Shimadzu spectrometer, ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer using TMS as internal standard. HR-MS spectra were recorded in MALDI-TOF Mass Spectrometer. The progress of the reaction was monitored by TLC, and yields refer to isolated pure products.

Experimental Section

Preparation of catalyst WEB⁴⁵

The water extract of banana (WEB) has been prepared by drying the banana peels in sunlight at open atmosphere; burning the banana peels to ash. 5 g of banana peels ash was suspended in 100 mL distilled water in a beaker and stirred well for about 2 h at RT. The mixture was then filtered; and the filtrate was termed as water extract of banana (5%).

General experimental procedure

A mixture of aldehyde (1 mmol), malononitrile (1 mmol), and WEB (1.2 mL) taken in pestle and mortar was ground at RT for the appropriate time (4-10 min) till the completion of the reaction as monitored by TLC. Then 5 mL water was added to the reaction mixture, the solid separated filtered and the pure crystalline product recovered by recrystallization from absolute ethanol. The homogeneity of the compound is confirmed by FT-IR, ^1H and ^{13}C NMR spectra. Melting points of the synthesized products have been compared with literature.

Spectral data of some compounds

2-(Phenylmethylene) malononitrile (Table I, Entry 1): Yield 93%. m.p. 81-83°C (Lit. 82-83°C). FT-IR (KBr): 3033 (HC=C), 2219 (CN), 1580 cm^{-1} (C=C); ^1H NMR (300 MHz, CDCl_3): δ 7.93-7.96 (d, $J=8.5$ Hz, 2 H, phenyl), 7.82 (s, 1 H, CH), 7.54-7.66 (m, 3 H, phenyl).

2-[(4-Chlorophenyl) methylene] malononitrile (Table I, Entry 2): Yield 89%. m.p. 165°C (Lit. 163-165°C). FT-IR (KBr): 2223 (CN), 1582 cm^{-1} (C=C); ^1H NMR (300 MHz, CDCl_3): δ 7.85 (d, $J=8.4$ Hz, 2H, phenyl), 7.77 (s, 1H, CH), 7.52 (d, $J=8.4$ Hz, 2H, phenyl).

2-(4-Fluorophenylmethylene) malononitrile (Table I, Entry 4): Yield 85%. m.p. 123-125°C (Lit. 121- 23°C). ^1H NMR (400 MHz, CDCl_3): δ 7.97 (dd, $J=8.7, 5.2$ Hz, 2H), 7.77 (s, 1H), 7.25 (dd, $J=14.2,$

5.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.82, 158.42, 133.51, 133.42, 127.41, 117.32, 117.10, 113.62, 112.55, 82.36.

2-(4-N, N-Dimethylaminophenyl methylene) malononitrile (Table I, Entry 5): Yield 87%. m.p. 181-182°C (Lit. 180-181°C). FT-IR (KBr): 3435 (HC=C), 2924.5 (HC-C), 2203 (CN), 1613, 1522 (C=C), 1358, 1183 cm^{-1} (C-N); ^1H NMR (300 MHz, CDCl_3): δ 7.79 (2H, d, $J=9.15$ Hz, 2.88 Hz), 7.42 (1H, s, C=CH), 6.68 (2H, d, $J=9.22$ Hz and 2.82 Hz), 3.13 (6H, s, N-Me₂); ^{13}C NMR (100 MHz, CDCl_3): δ 157.97, 154.17, 133.71, 119.25, 115.91, 114.84, 111.58, 71.78, 40.02.

2-(4-Nitrobenzylidene)malononitrile (Table I, Entry 6): Yield 89%. m.p. 158-159°C (Lit. 157-59°C). ^1H NMR (400MHz, CDCl_3): δ 8.41 (d, $J=8.84$, 2H), 8.10 (d, $J=8.84$, 2H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.8, 150.4, 135.8, 131.3, 124.6, 112.6, 111.5, 87.5.

2-(2-Chlorobenzylidene)malononitrile (Table I, Entry 7): Yield 85%. m.p. 79-82°C (Lit. 80-82°C); ^1H NMR (400MHz, CDCl_3): δ 7.80 (d, $J=7.84$, 2H), 7.74 (s, 1H), 7.71 (d, $J=7.84$, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.4, 133.1, 131.8, 129.9, 129.6, 113.4, 112.3, 83.5.

2-[(4-Methoxyphenyl) methylene] malononitrile (Table I, Entry 9): Yield 88%. m.p. 115-116°C (Lit. 114-115°C). FT-IR (KBr): 2219 (CN), 1599 cm^{-1} (C=C); ^1H NMR (300 MHz, CDCl_3): δ 7.94 (d, $J=8.5$ Hz, 2H, phenyl), 7.61 (s, 1H, CH), 7.22 (d, $J=8.5$ Hz, 2H, phenyl), 3.8 (s, 3H, OCH₃).

Conclusion

We have developed a simple, greener, efficient and economical approach for the synthesis of a series of benzylidene malononitrile derivatives from the Knoevenagel condensation of aryl/heteroaryl aldehydes and malononitrile using WEB under grindstone method. The advantages of the present approach are, it is an environmentally benign and safe protocol that includes a simple reaction set-up which does not require any special equipment, the reaction works at RT, excellent product yield, easier work-up, short reaction time and elimination of organic solvents. All synthesized Knoevenagel products (entries 1-12) were characterized and confirmed by FT-IR (Figure 2), ^1H , ^{13}C NMR and HR-MS (Figure 3) spectra.

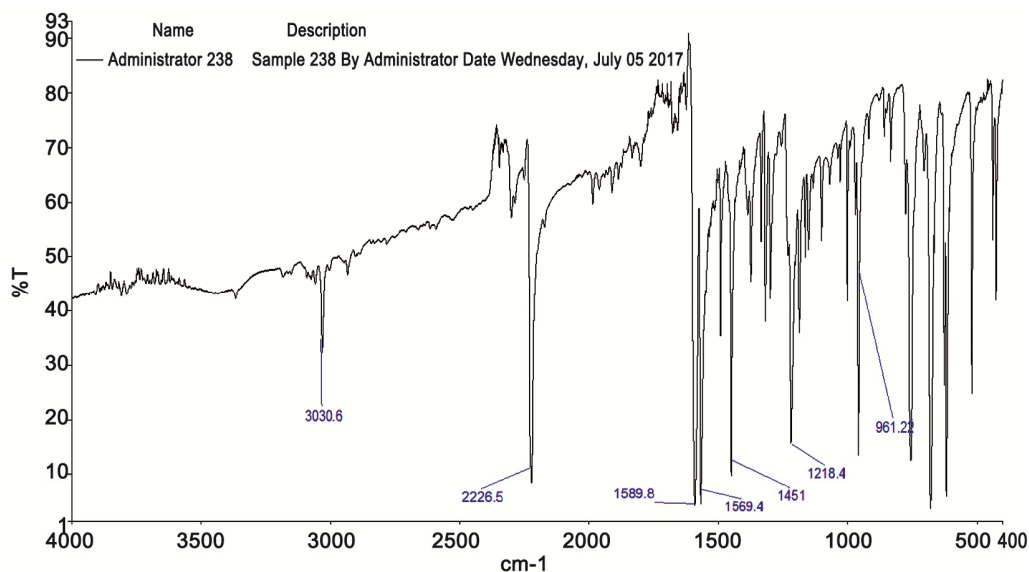


Figure 2 — FT-IR spectra of 2-(phenylmethylene) malononitrile

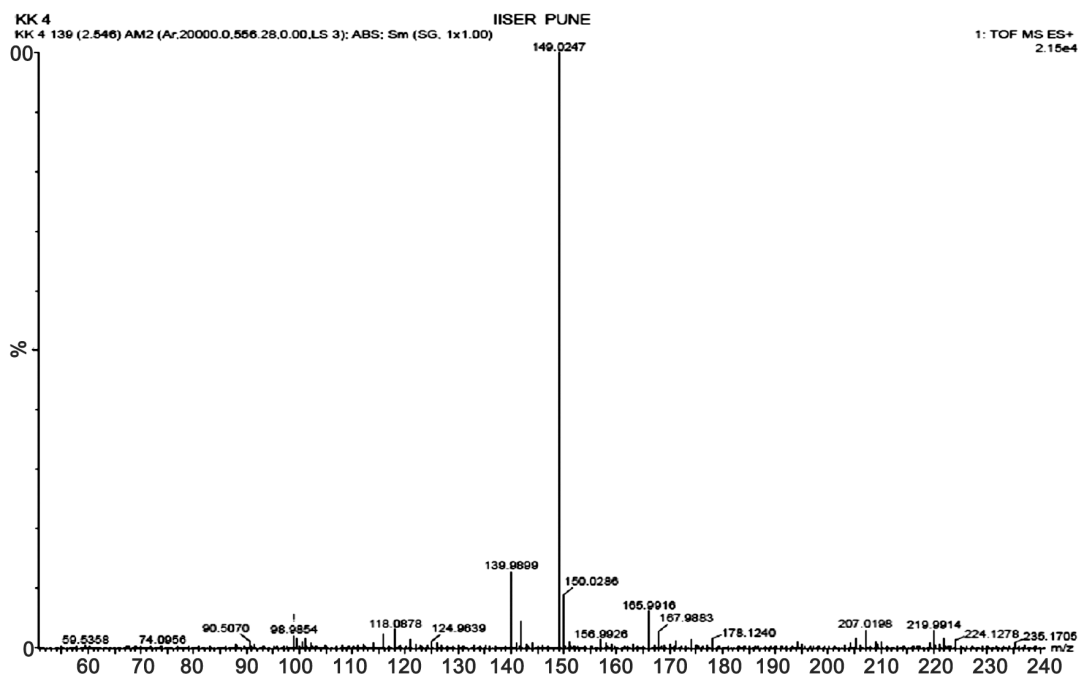


Figure 3 — HR-MS spectra of 2-(phenylmethylene) malononitrile

Supplementary Information

Supplementary information is available in the website <http://nopr.niscair.res.in/handle/123456789/60>.

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