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An alternative, practical, and ecological protocol for synthesis of arylidene analogues of Meldrum's acid as useful intermediates

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Abstract

This paper presents an ecological protocol for Knoevenagel condensation using a catalytic amount of 4,4′-trimethylenedipiperidine as a versatile, efficient, safe, commercially available, inexpensive, and recyclable organocatalyst by a ball-milling process at room temperature. The scope of the present protocol was explored and demonstrated for Knoevenagel condensation of the active methylene, such as Meldrum's acid with various aryl and heteroaryl aldehydes. The developed protocol provides a good to excellent conversion of various aldehydes to respective Knoevenagel products in an environmentally friendly process. Furthermore, this efficient process displays a combination of the synthetic virtues of conventional Knoevenagel condensation with ecological benefits and the convenience of a facile mechanochemistry procedure.

Keywords Versatile intermediate · C–C coupling · Heterogeneous catalysis · Solid-state reactions · Waste prevention

Introduction

Mechanochemistry and the ball milling process have been developed as clean and solvent-free approaches to chemical transformations and organic synthesis which can minimize usage of toxic, flammable, and volatile organic solvents and reduce environmental pollution [1]. In addition, the ball milling process fits well with the principles of green chemistry and the industrial processes. It often leads

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to improvements in the chemical reactions, including a reduced amount of catalyst loading, shorter reaction time, and higher yield [2].

Knoevenagel condensation is a well-known reaction for the formation of a carbon–carbon double bond that is widely used both in academic organizations and in the agrochemical, pharmaceutical, and perfume industries [3–5]. The Knoevenagel products are important reagents and versatile building blocks in organic synthesis both as intermediates and final products [6].

Arylidene analogues of Meldrum's acid are versatile substrates for various kinds of reactions [7, 8] and well-known intermediates for the synthesis of heterocyclic compounds of biological importance such as cardiotonics [9], anti-proliferative and HIV integrase inhibitory activities [10, 11], and in vitro antimalarial and antioxidant properties [12]. They are used to generate 3-arylpropanoic acids from the corresponding benzaldehydes [13].

As a consequence of this popularity, a number of protocols are being continuously developed for this useful conversion [14]. In general, the Knoevenagel condensation reaction is carried out in organic solvents using organic bases as catalysts, such as aliphatic amines or their corresponding ammonium salts, urea, ethylenediamine, dimethylamine, pyrrolidine, 2-methylpiperidine, and piperidine, and the amino acids glycine, β-alanine, or DL-proline [5, 15, 16]. Most of these catalysts have disadvantages, including being extremely or highly flammable liquids, gases, or vapors, harmful to aquatic life with long-lasting effects, toxic or explosive if heated, and may cause an allergic skin reaction or asthma symptoms. Hence, the development of an environmentally friendly, metal-free solid base, and sustainable catalytic protocol for Knoevenagel condensation which can tolerate a wide variety of functionality is still highly demanded. Also, the design and development of new reagents and catalysts for conducting organic reactions play important roles in organic synthesis and provide a useful and broad area for selectivity.

In pursuit of our interest in the solvent-free organic transformations using safe and green catalysts [17–19], we recently used planetary ball milling for the synthesis of Schiff bases [20, 21]. To circumvent the problems associated with using toxic, highly flammable, and volatile base catalysts such as piperidine, dimethylamine, pyrrolidine, and 2-methylpiperidine, herein, a simple and efficient Knoevenagel mechanocondensation protocol is developed. The structure of 4,4′-trimethylenedipiperidine (TMDP) bearing two piperidine rings linked by a 3-carbon spacer encouraged us to believe that TMDP can catalyze Knoevenagel condensation. TMDP is non-toxic, inflammable, highly thermally stable, inexpensive, commercially available, easy to handle and store, and recyclable. The aforementioned properties of TMDP as a solid organocatalyst along with the easy separation and purification of the Knoevenagel products in good to excellent yields are attractive features for this current protocol. To the best of our knowledge, no report has been presented on Knoevenagel reaction using TMDP as an organocatalyst through the ball milling process; moreover, TMDP has never been applied as an organocatalyst in organic chemistry. The results promise wide applicability of TMDP as an ecological and economical organocatalyst for typical C–C bond-formation processes through solid- or melt-state milling processes instead of piperidine which is toxic and a highly flammable liquid and vapor.

Results and Discussion

Thermal stability of TMDP

Herein, thermal analysis of TMDP is studied for the first time. Differential scanning calorimetry (DSC) was performed on TMDP to determine its melting and boiling points or decomposition onset temperatures. The thermal behavior of TMDP is displayed as a DSC plot in a temperature range from 30 to 500 °C in Fig. 1. In nitrogen atmosphere, two sharp and one broad endothermic peak centered around 58, 332, and 110 °C on the DSC curves of TMDP were recorded, and no exothermic peak was observed. The first peak is likely due to the melting of TMDP which began at 52.3 °C and ended at 66.6 °C with a latent heat of fusion of 196.88 J g^{-1} (41.42 kJ mol^{-1}). According to the melting point definition of pure non-polymeric compounds based on DSC as the onset temperature of the first endotherm, the melting point of TMDP is 52.3 °C which is very different from that was reported in the literature (65–68.5 °C; Sigma Aldrich). Then, an endothermic broad peak is observed in the range 76–157 °C, which can be attributed to desorption of inherent moisture and physically adsorbed water in TMDP with a latent heat of desorption of 70.01 J g^{-1} (14.72 kJ mol^{-1}). The onset of the third endothermic peak was seen at 313.8 °C, and its end-set was at 335.9 °C with a latent heat of evaporation of 427.84 J g^{-1} (90.00 kJ mol^{-1}). The boiling point of a pure compound is essential information necessary before any industrial implementation. The maximum temperature of the second sharp endothermic peak at 332.5 °C was assigned as the boiling point of TMDP which, apart from the appreciable loss of weight, shows a common feature due to the decreasing heat capacity of the sample, namely that the baseline

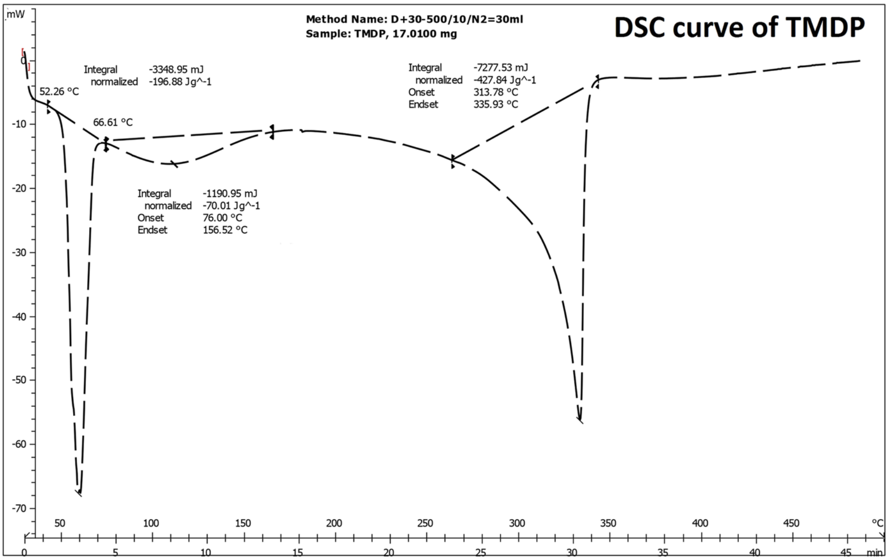


Fig. 1 DSC analysis of TMDP

shifts in the exothermic direction. The TMDP showed a relatively wide liquid range (> 280 °C), which melted at 52.3 °C, but did not begin to boil until it reached a temperature of 332.5 °C.

A thermogravimetric analysis/differential thermal analysis (TGA/DTA) curve of TMDP is presented in a temperature range from 30 to 800 °C in Fig. 2. Two peaks are visible on the DTA curve, and TMDP decomposition proceeds in one stage according to the TGA/DTG curve. The DTA curve of TMDP obtained by analysis in nitrogen atmosphere shows a broad peak below 126 °C with a maximum mass loss of 11.2%; this is attributed to the content of inherent moisture and physically adsorbed water in TMDP. The onset of temperature decomposition of TMDP was observed at 200.16 °C, and its thermal decomposition ended at 233.81 °C. The maximum mass loss of 88.6% was related to the total decomposition of TMDP. At 200–246 °C, completed. The thermal stability of organocatalysts plays an important role when their reactions need to be performed at high temperature. All the preceding results show that TMDP is thermally stable even at relatively high temperatures, and its thermal stability could be a consequence of the presence of hydrogen bonds in the structure of TMDP.

Knoevenagel condensation and catalytic efficiency of TMDP

In order to verify the catalytic performance of TMDP, it was used in the Knoevenagel condensation of aryl and heteroaryl aldehydes with Meldrum's acid as an active methylene. Initially, the condensation reaction between 4-chlorobenzaldehyde and Meldrum's acid was chosen as the model reaction to obtain the information on the optimal conditions (Table 1).

The model reactants were ground using the planetary ball mill at room temperature under catalyst- and solvent-free conditions. The 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (*2a*) was formed with 37% conversion after 60 min, indicating the requirement of a promoter for the reaction (Table 1, entry 1). Next,

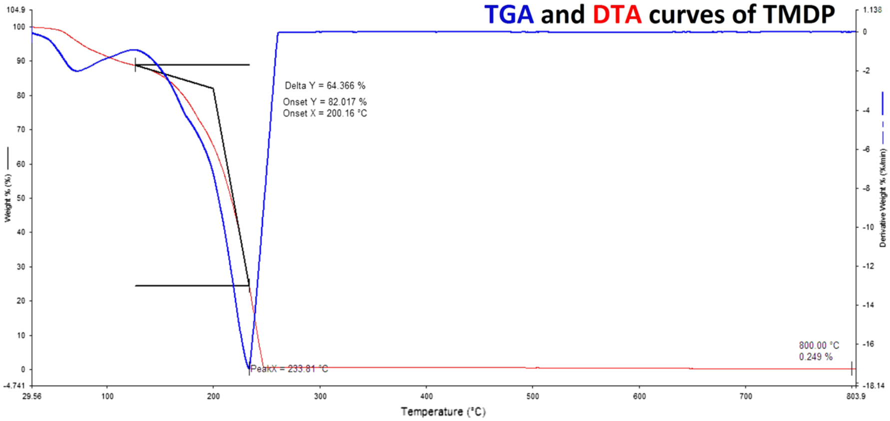


Fig. 2 TGA/DTA analysis of TMDP

Table 1 Condensation reaction of 4-chlorobenzaldehyde with Meldrum's acid at different conditions

Entry	Loading TMDP (mol%)	Number of milling balls	Speed (rpm)	Ball mill diameter (mm)	Milling time (min)	Conversion (%)
1	0	4	600	5	60	37
2	5	4	600	5	60	78
3	10	4	600	5	60	100
4	**10**	**4**	**600**	**5**	**10**	**100**
5	10	4	600	5	5	72
6	15	4	600	5	5	75
7	10	4	400	5	10	78
8	10	2	600	5	10	56
9	10	2	600	7	10	76

Reaction conditions: 4-chlorobenzaldehyde **1a** (5.0 mmol), Meldrum's acid (5.0 mmol), room temperature.

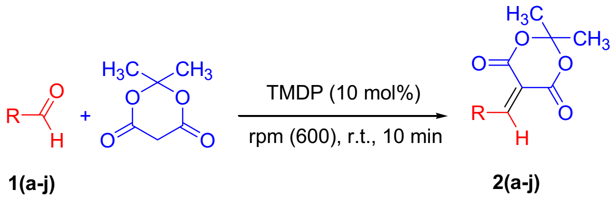
Bold data indicate optimized reaction conditions

the model reactants were milled in the presence of TMDP (5 mol%) at room temperature for 60 min under identical conditions to afford the (*2a*) with 78% conversion (Table 1, entry 2). A significant improvement was observed in conversion by increasing of TMDP loading (Table 1, entry 3).

The conversion remained constant when the reaction time was curtailed to 10 min (Table 1, entry 4), while further decreasing of the reaction time to 5 min led to a severe drop in conversion of **2a** (Table 1, entry 5). Also, the increasing of TMDP loading up to 15% led to 75% conversion after 5 min (Table 1, entry 6). The results exhibited that the technical parameters such as revolution per minute (rpm), size, and number of ball millings play important roles in performing Knoevenagel condensation (Table 1, entries 7–9). We selected entry 4 in Table 1 as the optimized reaction conditions.

The scope and generality of the current protocol for the Knoevenagel condensation was evaluated through the reaction of various aldehydes **1**(**a–j**) and Meldrum's acid using planetary ball milling under optimized reaction conditions (Scheme 1).

A broad range of the arylidene analogues of Meldrum's acid was isolated in good to excellent yield under optimal reaction conditions (Table 2). The reaction was found to be compatible with diverse functional groups such as halogen, ether, nitro, and hydroxyl (Table 2, entries 1, 4, 5, and 10). Furfural gave the desired



Scheme 1 Knoevenagel condensation of various aldehydes **1**(**a–j**) and Meldrum's acid

Table 2 Knoevenagel condensation of various aryl aldehydes with Meldrum's acid in the presence of TMDP under optimized reaction conditions

Entry	Aldehydes **1(a–j)**	Knoevenagel product **2(a–j)**	Yield (%)[a]	Melting point (°C)	
				Found	Reported [refs.]
1	4-Cl–C_6H_4–	2a	90	159–161	156–158 [22]
2	C_6H_5–	2b	87	84–85	84 [22]
3	4-CH_3–C_6H_4–	2c	85	157–158	150 [22]
4	4-CH_3O–C_6H_4–	2d	82	122–123	120–122 [22]
5	4-NO_2–C_6H_4–	2e	95	213–214	217–218 [23]
6	Furan–2–yl	2f	78	92–93	92 [22]
7	Thiohen–2–yl	2g	86	193–194	196–197 [24]
8	C_6H_5–CH=CH–	2h	81	105–106	109 [22]
9	4-$(CH_3)_2N$–C_6H_4–	2i	82	165–166	170 [22]
10	4-OH–C_6H_4–	2j	88	193–194	192–193 [25]

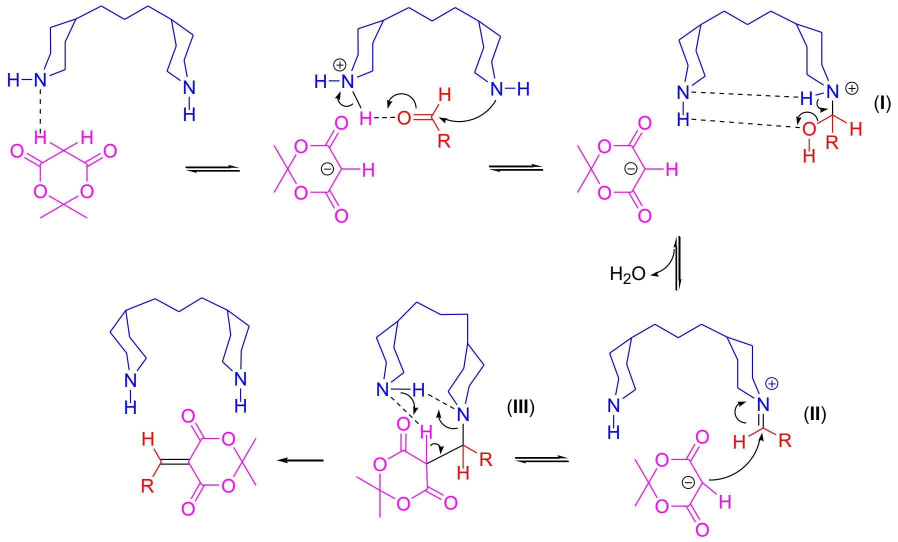
Reaction conditions: aldehydes **1**(**a**–**j**) (5.0 mmol), Meldrum's acid (5.0 mmol), TMDP (0.5 mmol), six balls with diameter 7 mm, revolution rate (600 rpm), room temperature, milling time (30 min)

[a] Isolated yield

Knoevenagel product in 78% yield without the formation of side products, which are normally observed under strongly acidic or basic conditions (Table 2, entry 6). No isomerization for conjugated aldehydes such as cinnamaldehyde was observed in the presence of TMDP under optimized conditions (Table 2, entry 8). Aldehydes bearing electron-withdrawing substituents afforded a slightly higher yield of the Knoevenagel products than electron-donating substituents at the same position due to increasing the electrophilicity of the carbonyl group (Table 2, entries 1 and 5 vs. 3, 4, 9, and 10).

On completion of the reaction, the TMDP could be separated and recovered by washing with deionized water followed by evaporation of water from an aqueous solution containing TMDP. The recovered organocatalyst was successfully used for three subsequent runs with an average 88% yield of **2a** which approved the recyclability of TMDP in this current protocol.

Based on the theoretical and experimental reports in the literature [26], a possible mechanism is postulated and illustrated in Scheme 2. In this mechanism, TMDP acts both as a nucleophile toward the aldehyde and as a base toward the active methylene, involving the corresponding iminium intermediate (**II**) as the acceptor (Scheme 2). The first step includes the formation of the carbinolamine intermediate (**I**) through the attack of piperidine to the carbonyl group and participation of the second piperidine moiety as base to activate methylene compound, leading to a lower free-energy barrier for the formation of the carbinolamine intermediate (**I**). The second reaction step is the elimination of water from carbinolamine intermediate (**I**) which lead to the formation of two charged species, including iminium ion (**II**) and the deprotonated active methylene. It is speculated that the piperidine moieties of TMDP act both as a nucleophile toward the aldehyde and as a base toward the active methylene. The nucleophilic attack of deprotonated active methylene to iminium ion (**II**) led to the formation of the



Scheme 2 A possible mechanism of the Knoevenagel condensation of various aldehydes **1**(**a–j**) and Meldrum's acid in the presence of TMDP

intermediate (**III**) followed by proton exchange with the TMDP which afford the Knoevenagel product.

The feasibility of the present method on a gram-scaled experiment was performed with 4-chlorobenzaldehyde (7.03 g, 50 mmol) and Meldrum's acid (7.21 g, 50 mmol) using TMDP (2.10 g, 10 mol%) under optimized reaction conditions which afforded 11.2 g of **2a** (84% isolated yield) within 10 min, almost similar in all respects with the mmol-scale entry.

Then, the catalytic efficiencies of TMDP, triethylamine, and piperidine were compared under the aforementioned optimized conditions which gave the desired product **2a** in 90, 41, and 52% yields, respectively. Lesser yield obtained with the use of triethylamine and piperidine signified the role of the number of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) sites in promoting the Knoevenagel condensation. A benefit of utilizing TMDP over piperidine is its safety and non-toxicity. The lower volatility of TMDP, as compared to piperidine or pyridine, allows it to be safely handled by less experienced chemists. Also, a cleaner reaction and multiple rounds of recycling justify its higher cost compared to piperidine.

Experimental

General

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. The known products were characterized by their melting point, ^{1}H NMR, and ^{13}C

NMR. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates. In all the cases, the ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 400 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Ball milling was performed in a Retsch PM100 planetary ball mill using a stainless-steel chamber and four or six stainless steel balls (diameter: 5 or 7 mm) with 300–600 revolutions per minute (rpm). Differential scanning calorimetry (DSC) curves were obtained with the use of a DSC-Mettler Toledo DSC 822e calorimeter. The measurements were taken in the aluminum pans with a pierced lid with the sample mass 17.01 mg under a dry nitrogen gas atmosphere (30 mL min^{-1}). Dynamic scans were performed at a heating rate of 10 °C min^{-1} in the temperature range 30–500 °C. TGA/DTA curves were obtained with the use of a Mettler Toledo TGA/SDTA 851e. All measurements were taken in the Al_2O_3 crucible with the sample mass 6.81 mg under nitrogen atmosphere (30 mL min^{-1}). Dynamic scans were performed at the heating rate of 10 °C min^{-1} in the temperature range 30–800 °C.

Typical procedure for the synthesis of arylidene analogues of Meldrum's acid in the presence of TMDP

The aldehyde (5.0 mmol), Meldrum's acid (5.0 mmol), and TMDP (10 mol%) were ground vigorously using four milling balls with a diameter of 5 mm at 600 rpm for 10 min at room temperature. Then, 10 mL of water was added to the grinding jar, TMDP was separated by filtration, and after evaporation, solvent was reused in the subsequent runs. The crude material was purified by column chromatography (95:5 hexane/EtOAc) to give the corresponding Knoevenagel products. The physical (melting point) and spectroscopic data (^{1}H NMR) of all the known Knoevenagel products [2(**a**–**j**)] were in good agreement with that reported in the literature [22–25].

^{1}H NMR of the known products

5-(4-Chloro-benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (***2a***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.37$ (s, 1H), 8.02 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 1.80 (s, 6H) ppm.

5-Benzylidene-2,2-dimethyl-1,3-dioxane-4,6-diones (***2b***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.34$ (s, 1H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.04 (t, $J = 8.0$ Hz, 2H), 6.89 (t, $J = 8.0$ Hz, 1H), 1.69 (s, 6H) ppm.

2,2-Dimethyl-5-(4-methylbenzylidene)-1,3-dioxane-4,6-diones (***2c***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.36$ (s, 1H), 8.01 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 2.42 (s, 3H), 1.78 (s, 6) ppm.

5-(4-Methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (***2d***): ^{1}HNMR (400 MHz, $CDCl_3$) $\delta = 8.38$ (s, 1H), 8.24 (d, $J = 8.0$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 3.91 (s, 3H), 1.79 (s, 6H) ppm.

2,2-Dimethyl-5-(4-Nitro-benzylidene)-1,3-dioxane -4, 6-dione (***2e***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.45$ (s, 1H), 8.31 (d, $J = 8.6$ Hz, 2H), 8.05 (d, $J = 8.6$ Hz, 2H), 1.85 (s, 6H) ppm.

5-Furan-2-ylmethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (***2f***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.45$ (d, $J = 3.6$ Hz, 1H), 8.34 (s, 1H), 7.83 (s, 1H), 6.73 (d, $J = 3.5$ Hz, 1H), 1.76 (s, 6H) ppm.

2,2-Dimethyl-5-(thiophen-2-ylmethylene)-1,3-dioxane-4,6-dione (***2g***): ^{1}HNMR (400 MH, $CDCl_3$) $\delta = 8.65$ (s, 1H), 8.01 (d, $J = 4.0$ Hz, 1H), 7.89 (d, $J = 4.0$ Hz, 1H), 7.27-7.24 (m, 1H), 1.77 (s, 6H) ppm.

2,2-Dimethyl-5-(3-phenyl-allylidene)-1,3-dioxane-4,6-dione (***2h***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.33$-8.31 (m, 1H), 8.18 (d, $J = 12.0$ Hz, 1H), 7.66 (m, 2H), 7.43-7.41 (m, 4H), 1.76 (s, 6H) ppm.

5-(4-Dimethylamino-benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (***2i***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.29$-8.21 (m, 3H), 6.69 (d, $J = 9.5$ Hz, 2H), 2.48 (s, 6H), 1.76 (s, 6H) ppm.

5-(4-Hydroxy-benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (***2j***): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 10.92$ (s, 1H), 8.28 (s, 1H), 8.12 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 1.75 (s, 6H) ppm.

Conclusion

In summary, an efficient protocol has been developed for Knoevenagel condensation using TMDP as a new organocatalyst under mild and solvent-free conditions which is considered a clean and ecological procedure. The aldehydes **1a–j** were reacted with Meldrum's acid in the presence of catalytic amounts of TMDP using planetary ball milling at room temperature. The Knoevenagel products were obtained in high to excellent yields under the optimized conditions. This work represents, to the best of our knowledge, the first study of the catalytic efficiency of TMDP in Knoevenagel condensation through the milling process at room temperature in a short reaction time under solvent-free conditions. This current protocol can be considered as an ecological and economical method because TMDP is solid, non-toxic, inexpensive, commercially available, recyclable, with easy handling and storage. The achieved experimental data showed that TMDP can be used as a green and safe alternative reagent instead of piperidine in organic synthesis under mild conditions, and we hope that our work will encourage further research in this area with promising results for future applications of TMDP in both academic and industrial processes. Further studies are currently in progress to broaden the potential catalytic activity of TMDP in other organic reactions and will be reported as appropriate.

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Compliance with ethical standards

Conflicts of interest There are no conflicts of interest to declare.

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