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ORIGINAL PAPER

Nanoammonium salt: a novel and recyclable organocatalyst for one-pot three-component synthesis of 2-amino-3-cyano-4*H*-pyran derivatives

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Abstract 1,3-Propanediaminium methanesulfonate [(PDA)($MeSO_3$)] was synthesized as the first nanoaliphatic ammonium salt via a safe and simple chemical route in aqueous media. [(PDA)($MeSO_3$)] ammonium salt was characterized by XRD, TEM, SEM, EDS, DLS, AFM, ^{1}H NMR, ^{13}C NMR, FT-IR, TG, and elemental analysis. [(PDA)($MeSO_3$)] ammonium salt was efficiently applied as an eco-friendly and recyclable organocatalyst for the one-pot, three-component synthesis of 2-amino-3-cyano-4*H*-pyran derivatives. From an economical and environmental point of view, this novel catalyst has the merits of environmental friendliness, high yields, shorter reaction time, simple work-up, easy operation, the avoidance of the organic solvents, and inexpensive catalysts.

Keywords Ammonium salt · Nano · Organocatalyst · 2-Amino-3-cyano-4*H*-pyrans · Recyclability

Introduction

In the recent years, molten salts (ionic liquids) have received significant interest in organic synthesis as catalyst because of their special properties such as low vapor pressure, excellent thermal, chemical stability, nonflammability, tunable polarity, high ionic conductivity, and immiscibility with certain organic solvents. The widespread range of possible cation and anion combinations represents the various applications and tunable interactions [1, 2]. On the other hand, nanostructural materials due to their unique structural and textural properties have a broad range of potential uses in biomedical and biological fields [3, 4]. Also, the many reports have been found using nanostructural materials as efficient catalysts in chemical reactions [5, 6]. To benefit from the unique properties of molten salts and the valuable applications of nanocatalysts, very recently, Zolfigol and his co-workers have been reported the first nanomolten salt, namely 1-methylimidazolium tricyanomethanide [7]. Today's, the researchers have showed that imidazolium salts have moderate aquatic toxicity and their industrial applications are limiting due to expensive cost and high toxicity [8, 9]. Therefore, other classes of molten salts require to be analyzed more closely. Among the different molten salts, ammonium salts are well known and have wonderful industrial uses due to their bioactivity and surface activity [10–13]. Also, they were easily prepared from cheap starting materials.

4*H*-Pyran and its derivatives represent the key building blocks of many natural products and constitute the core of valuable compounds exhibiting a wide range of pharmacological and biological activities such as anticancer [14], antimicrobial [15], antioxidant [16], and antiproliferative properties [17]. The amino-4*H*-pyrans are often employed in pigments and cosmetics, or used as potentially biodegradable agrochemicals. In addition, the 4*H*-pyran derivatives bearing a nitrile functional group are useful intermediates for the synthesis of compounds such as 1,4-dihydropyridines, pyridones, pyranopyrazoles, imidoesters, aminopyrimidines, and lactones [18, 19]. Because of the important aforementioned properties of 4*H*-pyran derivatives, preparation of this heterocyclic nucleus has gained great significance in

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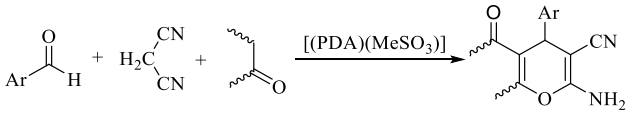
organic synthesis. Several methods have been reported for the one-pot synthesis of 2-amino-3-cyano-4*H*-pyran scaffold via a three-component condensation of aldehydes and alkylmalonates with carbonyl compounds possessing a reactive α-methylene group in the presence of heterogenous and homogenous catalysts such as PEG-SO_3H [20], tungstic acid functionalized mesoporous SBA-15 [21], nanosized zeolite clinoptilolite [22], KSF [23], CuO-CeO_2 [24], Mg/Al hydrotalcite [25], cetyltrimethylammonium chloride [26], egg shell [27], *S*-proline [28], alumina [29], KF/Al_2O_3 [30], imidazole [31], 4-dimethylaminopyridine [32], Et_3N, piperidine [33], morpholine [34], combined NaOAc/KF [35], tetraalkylammonium halides [36] or ionic liquids including [2-AEMIm] PF_6 [37], TMGT [38], and [cmmim]Br, [cmmim][BF_4] [39]. Although these protocols are valuable, they undergo one or more of the following disadvantages such as high temperature, low yields, long reaction times, using a large amount of toxic catalyst or solvents, and tedious work-up procedures. Therefore, it is still preferable to follow a green procedure applying a reusable nonhazardous catalyst for the efficient synthesis of 2-amino-3-cyano-4*H*-pyrans.

In continuing our efforts on the development of environmentally benign procedures by using efficient catalysts [40–45], herein, we have synthesized 1,3-propanediaminium methanesulfonate [(PDA)($MeSO_3$)] as the first nanoaliphatic ammonium salt in aqueous media (Scheme 1).

To explore the catalytic activity of [(PDA)($MeSO_3$)] ammonium salt in organic reactions, we have used it as a recyclable organocatalyst for the efficient one-pot, three-component synthesis of 2-amino-3-cyano-4*H*-pyran derivatives (Scheme 2).



Scheme 2 Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives catalyzed by [(PDA)($MeSO_3$)] nanoammonium salt

Experimental section

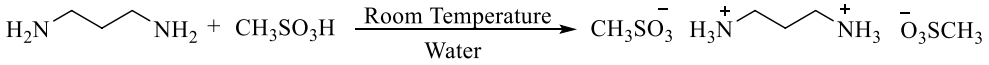
General information

Chemicals were purchased from Merck Chemical Company and used as received. Melting points were determined by Buchi 510 apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance DPX-400 using deutrated DMSO-d_6 and $CDCl_3$ as solvent and TMS as internal standard. The purity of the products and the progress of the reactions were accomplished by TLC on silicagel polygram SILG/UV254 plates. TEM analysis was performed using TEM microscope (Philips CM30). FT-IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). A Shimadzu thermogravimetric analyzer (TG-50) was applied to characterize the gravimetric (TG) behavior of the [(PDA)($MeSO_3$)] ammonium salt. Elemental analysis was carried out by a ECS4010 CHNSO analyzer. Power X-ray diffraction (XRD) patterns were obtained through a Bruker D8-advance X-ray diffractometer with Cu Ka (k = 0.154 nm) radiation. An atomic force microscopy (DME Model Igloo) was also utilized for AFM images. Morphologies of [(PDA)($MeSO_3$)] were observed using a scanning electron microscope (JSM-5600LV, JEOL Ltd., Japan) with an operating voltage of 3 kV. The elemental composition of catalyst was analyzed using an X-ray energy-dispersive spectroscopy (EDS) detector (IE 300X, Oxford, UK) attached to the SEM. The particle size distribution of nanoammonium salt was characterized by dynamic light scattering (DLS, $VASCO_3$-Cordouan) with cumulants method.

Typical procedure for the synthesis of [(PDA)($MeSO_3$)] nanoammonium salt

A solution of methanesulfonic acid (50 mmol, 4.805 g) in water (30 mL) was dropwisely added to an aqueous solution of 1,3-diaminopropane (50 mmol, 3.706 g) at room temperature. However, the stirring of the resultant solution was preserved for another 20 h at the same conditions. Then water was removed by distillation under reduced pressure, and the residue was dried at room temperature to reach up to [(PDA)($MeSO_3$)] as a shiny white solid.

1,3-Propanediaminium methanesulfonate [(PDA)($MeSO_3$)]. M.P: 157 °C; Yield: 96% (12.78 g); IR (KBr): υ 3200–2500, 1619, 1318, 1137, 595 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 7.86 (br, 6 H, NH_3), 2.88 (t, $^3J_{H-H}$ = 9.6 Hz, 4 H, CH_2), 2.42 (s, 6 H, CH_3), 1.86 (p, $^3J_{H-H}$ = 9.6 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 40.1, 36.5, 25.4.



Scheme 1 Synthesis of 1,3-propanediaminium methanesulfonate [(PDA)($MeSO_3$)]

General procedure for the synthesis of 2-amino-3-cyano-4H-pyran in the presence of [(PDA)($MeSO_3$)] nanoammonium salt

[(PDA)($MeSO_3$)] (10 mol%, 0.0266 g) was added to a stirred mixture of aldehyde (1 mmol), malononitrile (1 mmol) and carbonyl compound possessing a reactive α-methylene group (1 mmol). The reaction mixture was stirred at 60 °C for the appropriate time (Table 2). The progress of the reaction is monitored by TLC. After completion of the reaction, water (5 mL) was added to the reaction mixture and the resulted solid filtered and completely

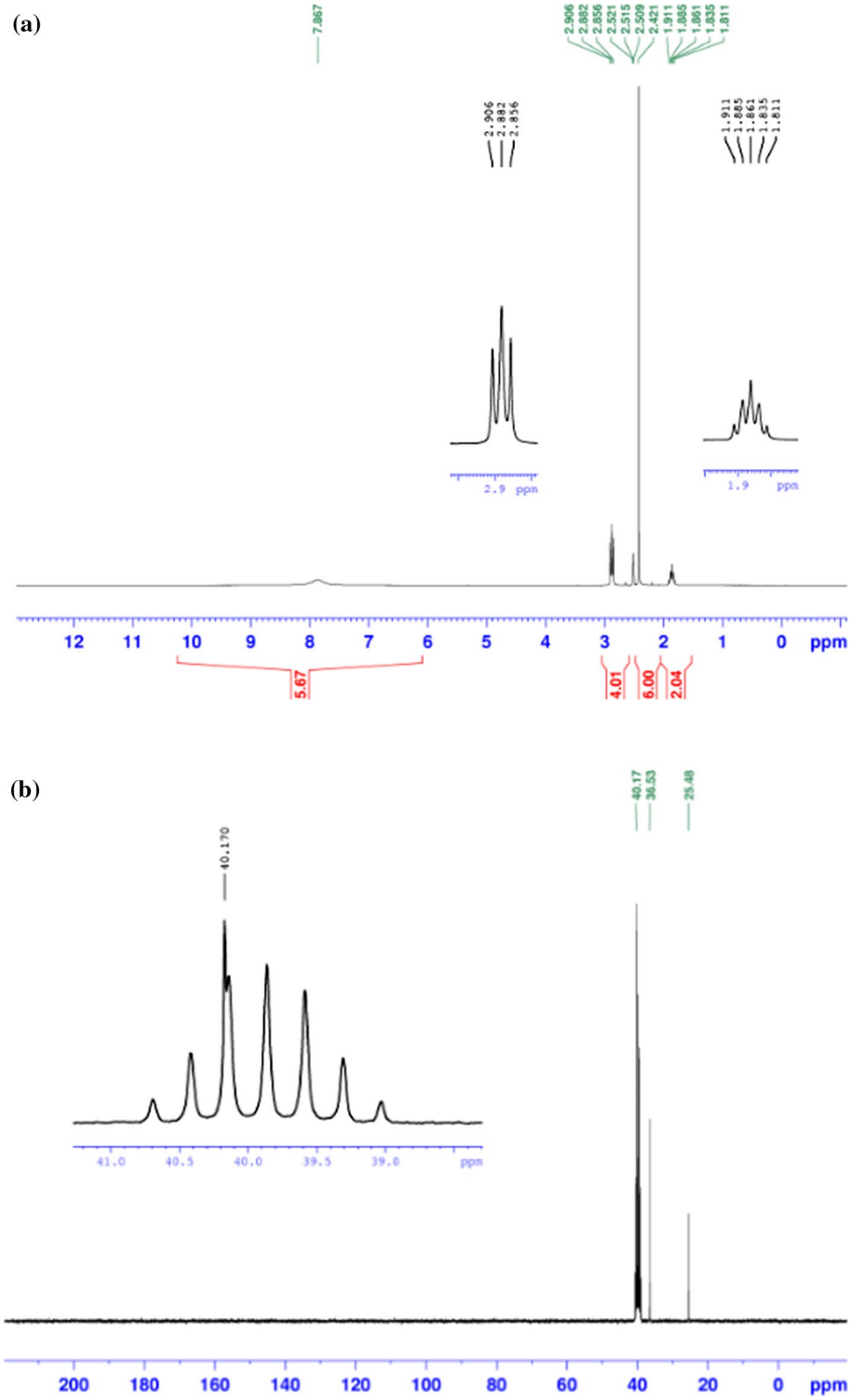


Fig. 1 **a** The ^{1}H NMR spectrum of [(PDA)($MeSO_3$)], **b** The ^{13}C NMR spectrum of [(PDA)($MeSO_3$)]

washed with H_2O (2 × 10 mL). Pure products were obtained by recrystallization in aqueous ethanol. Nanoammonium salt was recovered by evaporation of the filtrate and drying in vacuum at room temperature.

Spectral data of 2-amino-3-cyano-4H-pyran derivatives

7-Amino-1,3-dimethyl-5-(3-nitrophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d] pyrimidine-6-carbonitrile **(23)** The colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, 1 H, $^4J_{H–H}$ = 8 Hz, Ar), 8.14 (d, 1 H, $^4J_{H–H}$ = 1 Hz, Ar), 7.83 (d, 1 H, $^3J_{H–H}$ = 8 Hz, Ar), 7.68–7.64 (t, 1 H, $^3J_{H–H}$ = 8 Hz, Ar), 7.53 (s, 2 H, NH_2), 4.63 (s, 1 H, CH), 3.42 (s, 3 H, CH_3), 3.13 (s, 3 H, CH_3) ppm; IR (KBr) 3335, 3231, 2200, 1689, 1630, 1529, 1513, 1492 cm^{-1}.

7-Amino-5-(2,4-dichlorophenyl)-1,3-di-methyl-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano [2,3-d] pyrimidine-6-carbonitrile **(25)** The yellow crystals; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 2 H, NH_2), 7.81 (s, 1 H, Ar), 7.59 (d, $^3J_{H–H}$ = 8 Hz, 1 H, Ar), 7.38 (d, $^3J_{H–H}$ = 8 Hz, 1 H, Ar), 4.40 (s, 1 H, CH), 3.57 (s, 3 H, CH_3), 3.15 (s, 3 H, CH_3). ppm; IR (KBr): υ 3334, 3236, 2221, 1708, 1660, 1551, 1513, 1485 cm^{-1}.

Procedure for the reusability test of [(PDA)($MeSO_3$)] nanocatalyst

[(PDA)($MeSO_3$)] (10 mol%, 0.0798 g) was added to a stirred mixture of benzaldehyde (3 mmol), malononitrile (3 mmol), and dimedone (3 mmol). The reaction mixture was stirred at 60 °C for 8 min. Then, water (5 mL) was added to the reaction mixture and the resulted solid filtered and washed with H_2O (2 × 10 mL). Nanoammonium salt was recovered by evaporation of the filtrate and drying in vacuum at room temperature. [(PDA)($MeSO_3$)] was then reused at the same conditions as above for at least five reaction runs and delivered the corresponding product (**6**) in high yield.

Results and discussion

Synthesis and characterization of 1,3-propanediaminium methanesulfonate [(PDA)($MeSO_3$)] as a nanoammonium salt

1,3-Propanediaminium methanesulfonate [(PDA)($MeSO_3$)] was synthesized as a nanobifunctional ammonium salt from cheap and readily available starting materials. The important advantage of the synthesized nanocatalyst was related to a safe and simple procedure for its preparation. The possibility to use water as a standard "green" solvent for the synthesis of catalyst as well as a reaction medium was a salient feature. The synthesized [(PDA)($MeSO_3$)] nanoammonium salt was fully characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, FT-IR, TGA, XRD, SEM, TEM, DLS, EDS, and AFM.

The ^{1}H NMR and ^{13}C NMR spectra of [(PDA)($MeSO_3$)], in DMSO-d_6 are shown in Fig. 1. The main peaks of ^{1}H NMR spectrum of [(PDA)($MeSO_3$)] were attributed to NH of cationic moiety and CH_3 of anionic moiety detecting in δ = 7.86 and 2.42 ppm, respectively. The presence of a peaks in δ = 1.86 and 2.88 ppm was allocated to hydrogens of methylene group. Also, in ^{13}C NMR spectrum of [(PDA)($MeSO_3$)], carbons of anionic moiety were observed in δ = 40.1 ppm. Two peaks were appeared at δ = 36.5 and 25.4 ppm related to carbons of cationic moiety.

FT-IR spectra of [(PDA)($MeSO_3$)], 1,3-diamino propane and methanesulfonic acid are implied in Fig. 2. In the FT-IR spectrum of [(PDA)($MeSO_3$)], a broad peak centered at 2500–3200 cm^{-1} was attributed to stretching

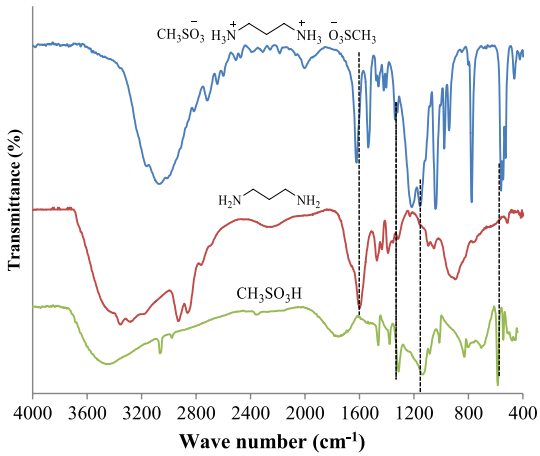


Fig. 2 FT-IR spectra of [(PDA)($MeSO_3$)], 1,3-diamino propane and methanesulfonic acid

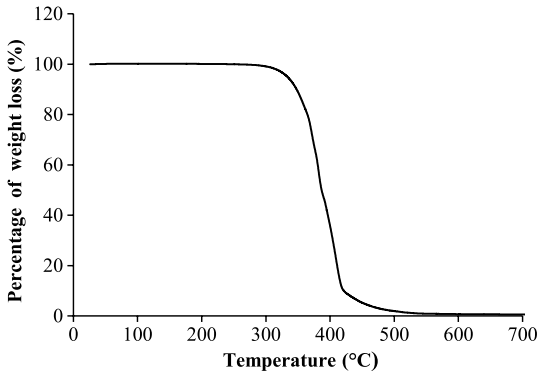


Fig. 3 Thermal gravimetric (TG) analysis of [(PDA)($MeSO_3$)]

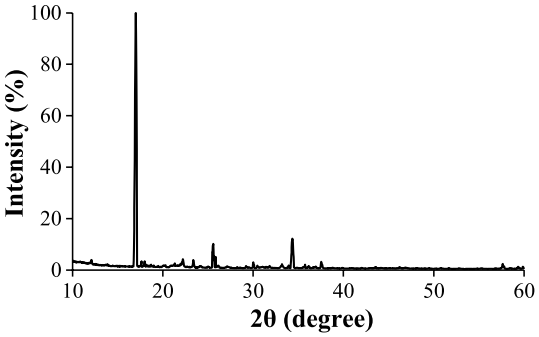


Fig. 4 XRD pattern of [(PDA)($MeSO_3$)]

vibrations of N–H (NH_3^+) bands. The peak was appeared at 1619 cm^{-1} in the spectra of [(PDA)($MeSO_3$)], and 1,3-diamino propane could be related to the bending vibrations of N-H bond. In the spectra of [(PDA)($MeSO_3$)] and methanesulfonic acid, two absorption peaks at 1318 and 1137 cm^{-1} were well assigned to the stretching vibrations of S=O bond. Also, the presence of a band at around 595 cm^{-1} was allocated to S–O stretching vibrations. These results were indicated that [(PDA)($MeSO_3$)] as ammonium salt was successfully synthesized.

The thermogravimetric (TG) analysis was used to determine the thermal stability of [(PDA)($MeSO_3$)] (Fig. 3). According to the TGA, the weight loss of [(PDA)($MeSO_3$)] nanoammonium salt was occurred in a single step after 287 °C was indicative of its good thermal stability up to 287 °C.

Size, shape, and morphology of [(PDA)($MeSO_3$)] as nanoammonium salt were studied through X-ray diffraction (XRD) pattern, scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), energy-dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM) analysis imaging demonstrations.

XRD patterns of [(PDA)($MeSO_3$)] in a domain of 10°–60° are illustrated in Fig. 4. As shown in Fig. 4, XRD patterns presented diffraction lines including high crystalline nature at $2\theta \approx 17.00°$, 25.48°, and 34.27°. The mean crystallite size was calculated via the Scherrer equation [$D = K\lambda/(\beta\cos\theta)$] (where D is the crystallite size, K is the shape factor, λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle in degree) and found to be in the nanometer range (15.1–31.0 nm).

SEM image and TEM image of [(PDA)($MeSO_3$)] are shown in Fig. 5. The particles size distribution of [(PDA)

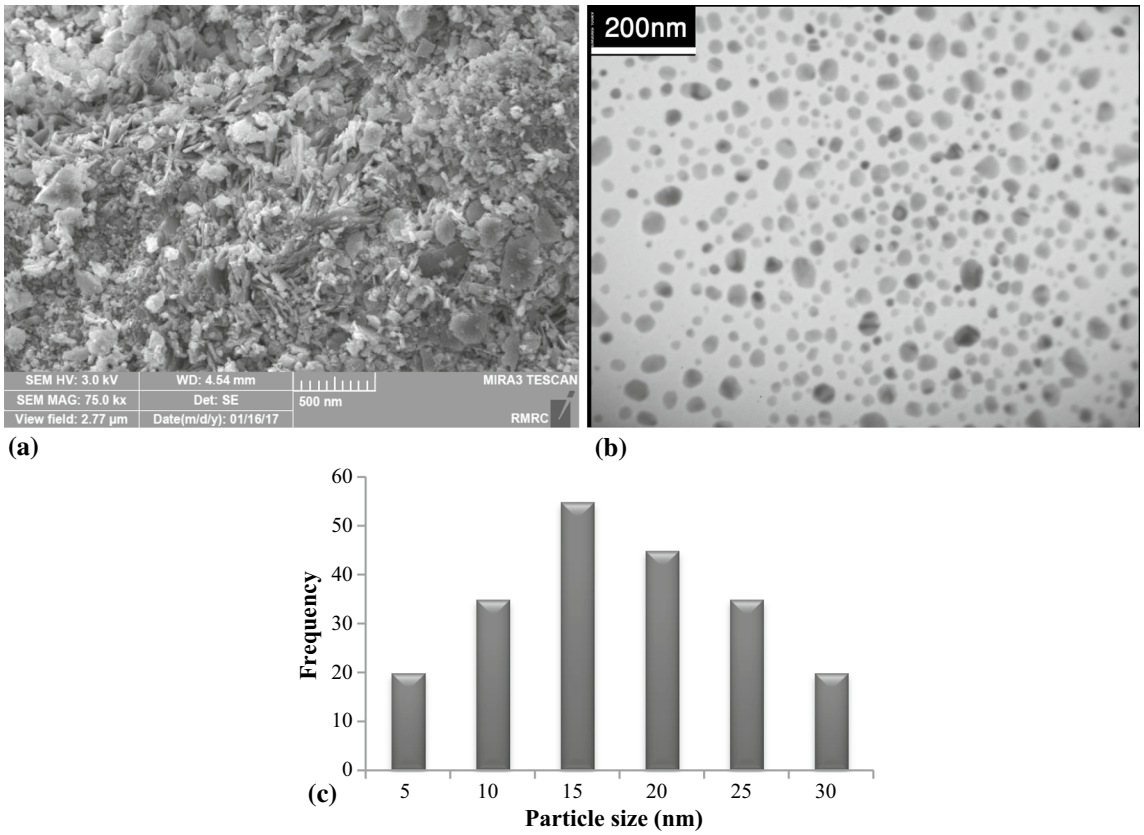


Fig. 5 **a** Scanning electron microscopy (SEM), **b** transmission electron microscopy (TEM) and **c** particles size distribution of [(PDA)($MeSO_3$)]

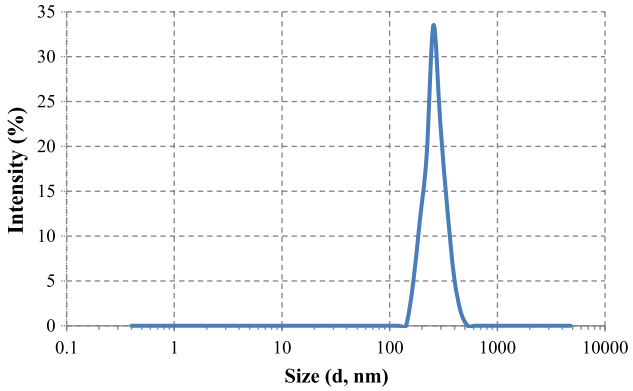


Fig. 6 Size distribution of [(PDA)($MeSO_3$)] by DLS

($MeSO_3$)] was evaluated using TEM and showed that the mean diameter of nanoparticles was about 15 nm. These results were in good agreement with the XRD results.

The particles size distribution of the [(PDA)($MeSO_3$)] was also investigated by dynamic light scattering (DLS) technique (Fig. 6). The hydrodynamic diameter of the particles was obtained in the range of 122–255 nm with the maximum peak around 164 nm by DLS that was about ten times larger than that obtained by TEM. This is due to the fact that the hydrodynamic nanoparticle diameter was measured in their dispersion situation, whereas TEM analyzed the particle core. Also, TEM gave the number average, while DLS provided the z-average of the diameter that was strongly affected by the presence of large particles [46].

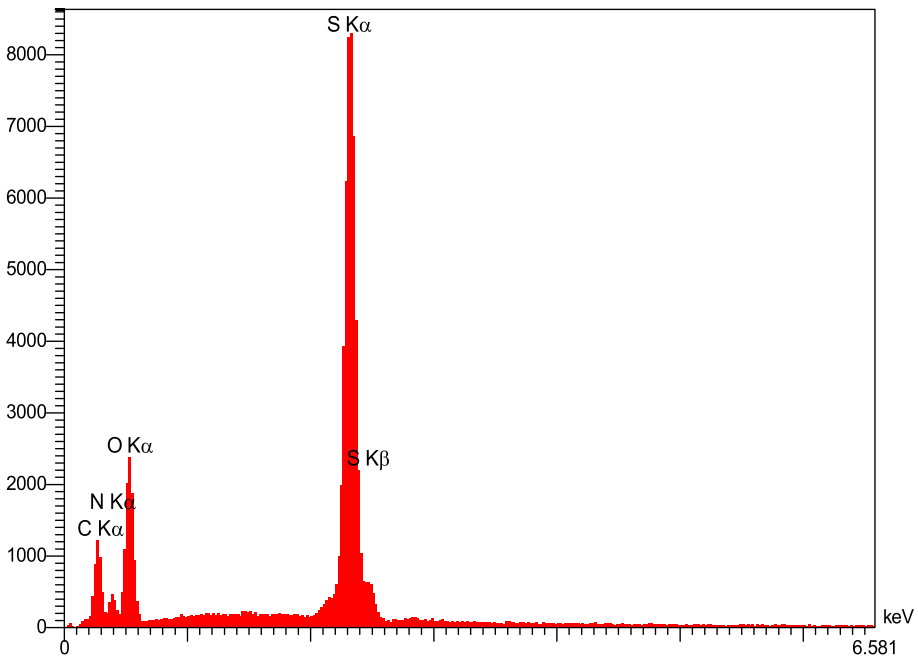
Energy-dispersive X-ray spectroscopy (EDS) analysis was used for structure identification [(PDA)($MeSO_3$)] ammonium salt (Fig. 7) and showed elemental composition of ammonium salt, including N, C, O, and S in which the obtained results were of acceptable concordance with the elemental analysis data (N = 10.54%, C = 22.58%, H = 6.79% and S = 24.10%).

The AFM images of [(PDA)($MeSO_3$)] were gave good information about surface morphology of nanoammonium salt. AFM images were derived from 1.1 μm * 1.1 μm scan part of the samples (Fig. 8). No key division area in size was identified in the illustrations. From three-dimensional 1.1 μm^2 × 1.1 μm framework, it came out that the achieved nanostructure ammonium salt showed an interrupted structure with a superior beyond planarity. In the surface conformation of the coat, [(PDA)($MeSO_3$)] was obviously detected with the size distribution 23–26 nm.

Catalytic activity of [(PDA)($MeSO_3$)] nanoammonium salt in the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives

The catalytic activity of the prepared nanoammonium salt was examined through the synthesis of 2-amino-3-cyano-4*H*-pyrans. For this purpose, initially, the reaction of benzaldehyde, malononitrile, and dimedone in the presence of 10 mol% of [(PDA)($MeSO_3$)] was chosen as a model reaction. The model reaction was investigated for the optimizing of the solvent, in the presence of different solvents such as acetonitrile, toluene, ethanol, water, and under solvent-free

Fig. 7 EDS spectrum of [(PDA)($MeSO_3$)]



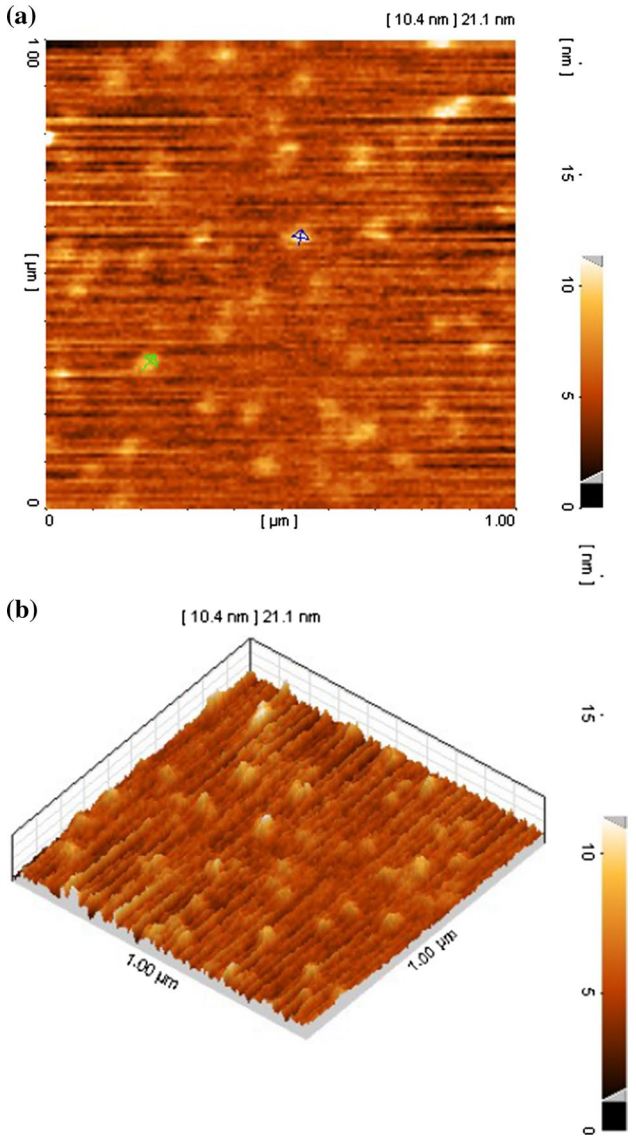


Fig. 8 **a** Two-dimensional and **b** three-dimensional AFM topography images of [(PDA)($MeSO_3$)]

conditions at 60 °C (Table 1, entries 1–5). As shown in Table 1, the best result was obtained under solvent-free conditions. A similar reaction at lower temperatures required longer reaction time and produced the desired product in lower yield (Table 1, entry 6). Further, no improvement was observed by increasing the reaction temperature from 60 to 80 °C in terms of reaction time and yield of the product (Table 1, entry 7). Similar reactions were performed in the presence of different catalytic amounts of [(PDA)($MeSO_3$)] at 60 °C under solvent-free conditions (Table 1, entries 8 and 9) and found that 10 mol% of the catalyst, which was used in the model reaction, was the best amount. The model reaction was also examined in the absence of the catalyst and low amount of the desired product obtained after 12 h. This result showed the importance of the presence of the catalyst for this reaction.

The generality and versatility of this method for the synthesis of 2-amino-3-cyano-4*H*-pyran derivatives were investigated by the reaction of malononitrile, various aldehydes and carbonyl compounds possessing a reactive α-methylene group under optimized reaction conditions (10 mol% of nanoammonium salt at 60 °C under solvent-free conditions). The results of these studies are summarized in Table 2.

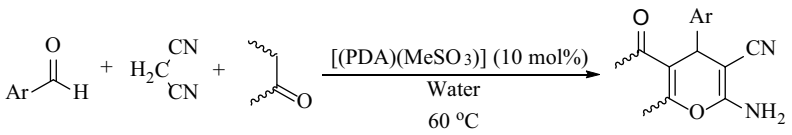
As indicated in Table 2, the reactions of substituted benzaldehydes bearing electron-releasing and electron-withdrawing groups with dimedone and malononitrile were proceed well and produced the corresponding products in good to high yields in short reaction times (Table 2, entries 1–5). To further expand the scope of the reaction, the use of diverse carbonyl compounds possessing a reactive α-methylene group [namely 1,3-cyclohexanedione, 4-hydroxycoumarine, 4-hydroxy-6-methyl-2-pyrone and 6-hydroxy-1,3-dimethylpyrimidine-2,4(1H,3H)-dione] was investigated. To our surprise, all they were easily transformed into the desired products in good to high yields in short reaction time (Table 2, entries 6–25).

Table 1 Synthesis of 2-Amino-4-benzoyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*chromene-3-carbonitrile under different conditions

Entry	Amount of catalyst (mol%)	Temperature (°C)	Solvent	Time (min)	Yield[a] (%)
1	10	60	–	8	95
2	10	60	Acetonitrile	40	81
3	10	60	Toluene	120	73
4	10	60	Ethanol	30	79
5	10	60	Water	10	92
6	10	40	–	120	88
7	10	80	–	8	95
8	5	60	–	25	84
9	20	60	–	8	95
10	–	60	–	12 h	10

[a] Isolated yields. Conditions: aldehyde (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol)

Table 2 Synthesis of 2-amino-3-cyano-4H-pyran derivatives in the presence of [(PDA)($MeSO_3$)] ammonium salt



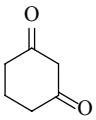
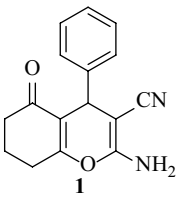
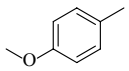
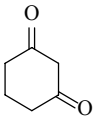
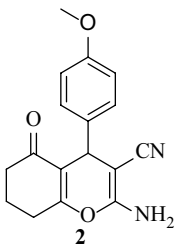
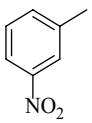
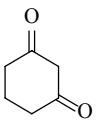
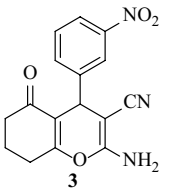
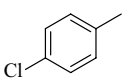
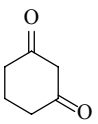
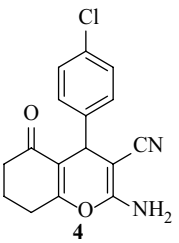
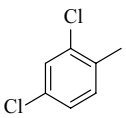
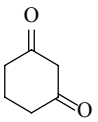
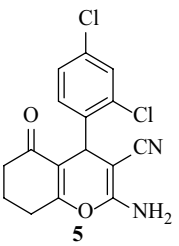
Entry	Ar		Product	Time (min)	Yield[a] (%)	Mp (°C) Found / Reported [ref]
1			 **1**	8	95	229–230 / 230–232 [47]
2			 **2**	6	93	190–191 / 192–194 [47]
3			 **3**	3	92	199–200 / 202–204 [47]
4			 **4**	4	91	225–226 / 224–226 [47]
5			 **5**	3	92	223–224 / 223–225 [47]

Table 2 continued

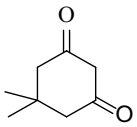
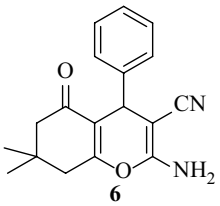
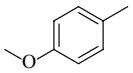
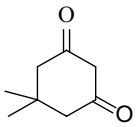
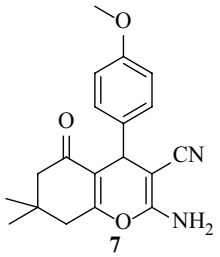
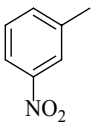
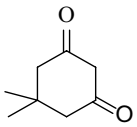
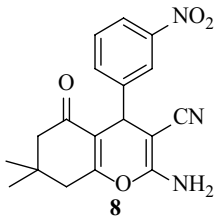
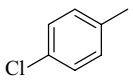
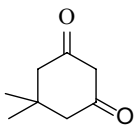
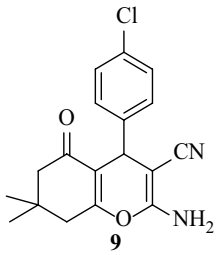
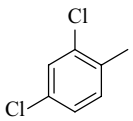
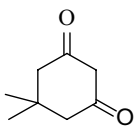
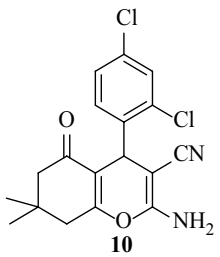
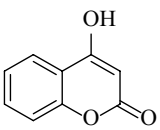
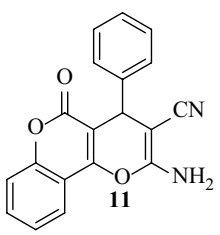
6			 **6**	5	95	230−231 / 227–229 [47]
7			 **7**	7	90	191−192 / 194–196 [47]
8			 **8**	3	98	212−213 / 212−214 [47]
9			 **9**	3	93	238 / 237−239 [47]
10			 **10**	3	94	114−115 / 115−117 [47]
11			 **11**	6	87	255−256 / 256−258 [36]

Table 2 continued

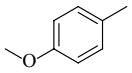
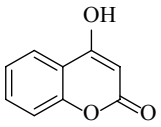
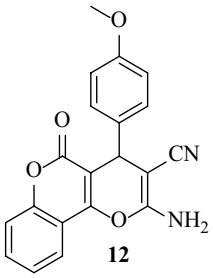
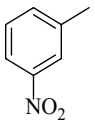
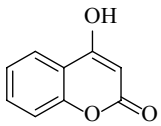
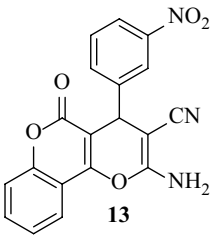
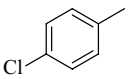
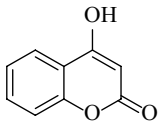
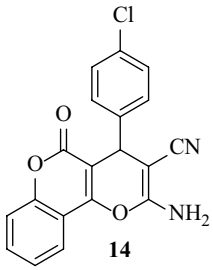
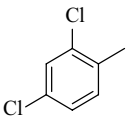
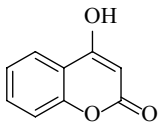
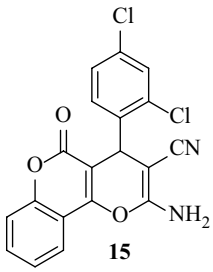
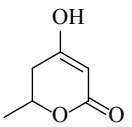
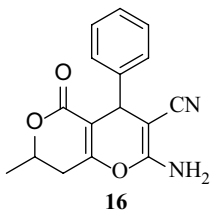
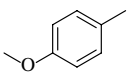
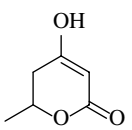
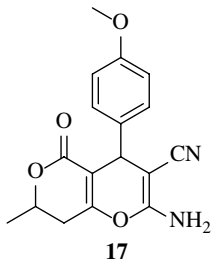
12			 **12**	10	82	238–239 / 240–242 [36]
13			 **13**	4	90	261–262 / 262–264 [36]
14			 **14**	5	86	264–265 / 263–265 [36]
15			 **15**	4	88	255–256 / 257–259 [36]
16			 **16**	7	88	220–221 / 223–225 [48]
17			 **17**	12	82	203 / 200–202 [48]

Table 2 continued

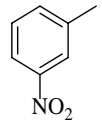
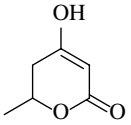
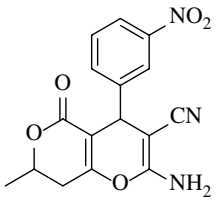
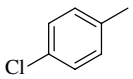
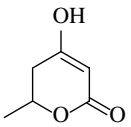
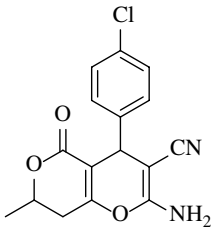
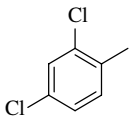
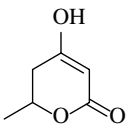
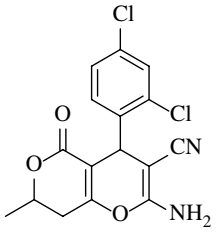
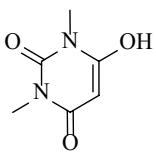
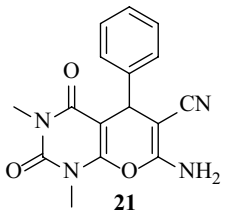
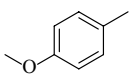
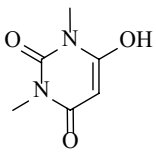
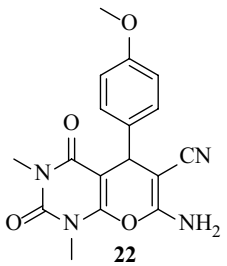
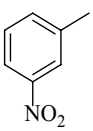
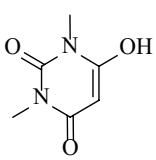
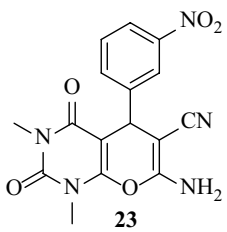
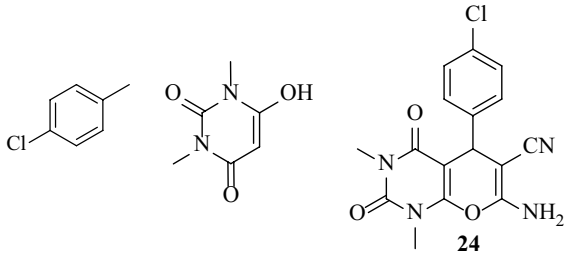
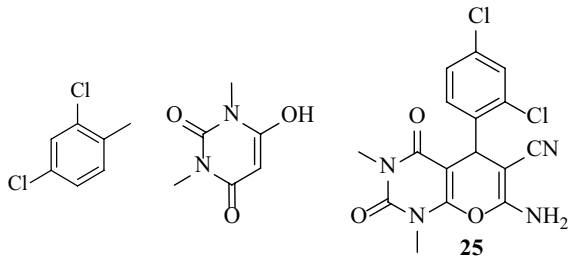
18			 **18**	5	92	230−231 / 234−236 [48]
19			 **19**	6	90	229−230 / 231−232 [30]
20			 **20**	5	90	230−231 / 234−235 [30]
21			 **21**	7	85	206−207 / 205−207 [48]
22			 **22**	15	80	225−226 / 226−227 [49]
23			 **23**	5	89	201−202 / 204 [49]

Table 2 continued

24	 **24**	6	85	240–242	243–244 [49]
25	 **25**	4	87	210–212	211–212 [49]

[a] Isolated yields. Conditions: aldehyde (1 mmol), malononitrile (1 mmol), carbonyl compound possessing a reactive α-methylene group (1 mmol), [(PDA)($MeSO_3$)] (10 mol%), 60 °C, solvent-free conditions

The recovery of [(PDA)($MeSO_3$)] ammonium salt in the reaction of benzaldehyde, malononitrile and dimedone was investigated in the presence of nanocatalyst (10 mol%) at 60 °C under solvent-free conditions. The reaction was very clean and the desired product obtained in excellent yield. After the completion of the reaction, since [(PDA)($MeSO_3$)] was completely soluble in water, water was subsequently added to the reaction mixture and the desired product filtered off and purified by recrystallization in ethanol. The nanoammonium salt was recovered after the evaporation of the filtrate. Therefore, nanoammonium salt could be completely isolated easily from the reaction mixture by simple filtration and reused for five cycles without significant loss in its activity (Fig. 9).

The comparison of TEM images and DLS of the used (Figs. 10, 11) with fresh catalyst (Figs. 5, 6) showed that the morphology and particle size of [(PDA)($MeSO_3$)] remained somewhat unchanged after five recovery times. Furthermore, the elemental analysis data (CHNS) confirmed the accuracy of the recovered catalyst.

The title methodology was cost-effective, environmentally friendly, and industrially important because of using reusable, eco-friendly, and inexpensive catalyst. These advantages for this high yielding condensation method offered ready scalability. For example, in the present investigation, the condensation of benzaldehyde, malononitrile, and dimedone in a 20 mmol scale in the presence of the [(PDA)($MeSO_3$)] nanocatalyst was investigated. As

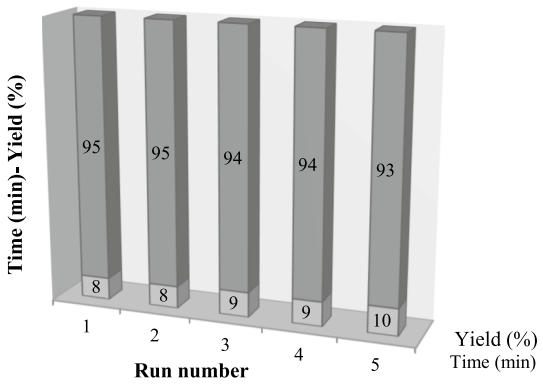


Fig. 9 Recycling experiment of [(PDA)($MeSO_3$)]

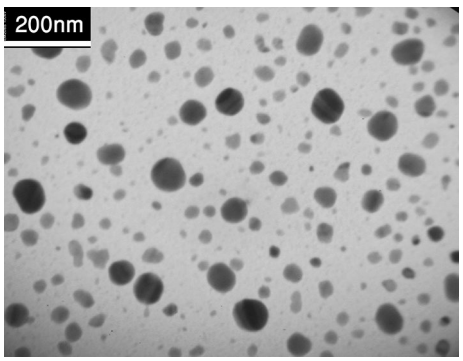


Fig. 10 TEM image of [(PDA)($MeSO_3$)] after five recovery times

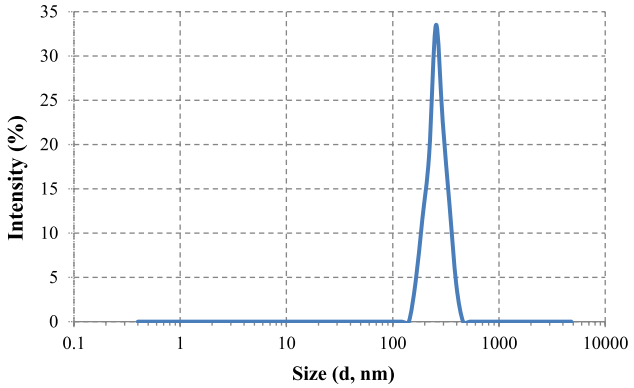


Fig. 11 Size distribution of [(PDA)($MeSO_3$)] by DLS after five recovery times

expected, the reaction proceeded similarly to the smaller scale, and the desired product was obtained at the same isolated yield and reaction time.

Conclusions

In summary, in this work, 1,3-propanediaminium methanesulfonate [(PDA)($MeSO_3$)] was synthesized as a novel bifunctional ammonium salt in water from cheap and readily available starting materials. The [(PDA)($MeSO_3$)] was fully characterized by various techniques. Catalytic application of [(PDA)($MeSO_3$)] as a recyclable and environmentally friendly nanocatalyst was studied in the one-pot, three-component synthesis of 2-amino-3-cyano-4*H*-pyran derivatives at 60 °C under solvent-free conditions. The most important advantages of this study were high yields, cleaner reaction profile, short reaction time, the avoidance of the organic solvents, and easy work-up. In addition to the above-mentioned advantageous, the use of a recyclable nanocatalyst was environmentally benign and cost-effective which made our methodology proper for the industrial goals.

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References

1. W. Sundermeyer, Angew. Chem. Int. Ed. Engl. **4**, 222 (1965)
2. O. Stenzel, H.G. Raubenheimer, C. Esterhuysen, *J. Chem. Soc. Dalton Trans*. (6), 1132 (2002)
3. B. Soghomon, F. Rasmus, in *Catalysis in Molten Ionic Media*, ed. by F. Lantelme, H. Groult (Elsevier Science, Amsterdam, 2013), pp. 131–158
4. S. Ravina, N.H. Singh, J. Biomed. Nanotechnol. **7**, 489 (2011)
5. K.A. Kuttiyiel, K. Sasaki, G.G. Park, M.B. Vukmirovic, L. Wu, Y. Zhu, J.G. Chen, R.R. Adzic, Chem. Commun. **53**, 1660–1663 (2017)
6. L.H. Wee, S.R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C.E.A. Kirschhocka, J.A. Martens, Chem. Commun. **46**, 8188 (2010)
7. M.A. Zolfigol, S. Baghery, A.R. Moosavi-Zare, S.M. Vahdat, H. Alinezhad, M. Norouzi, RSC Adv. **5**, 45037 (2015)
8. F. Bellina, C. Chiappe, M. Lessi, Green Chem. **14**, 148 (2012)
9. S. Studzińska, B. Buszewski, Anal. Bioanal. Chem. **393**, 983 (2009)
10. Z. Jia, D. Shen, w Xu, Carbohydr. Res. **333**, 1 (2001)
11. Y.H. Xiao, J.H. Chen, M. Fang, X.D. Xing, H. Wang, Y.J. Wang, F. Li, J. Oral Sci. **50**, 323 (2008)
12. W.L. Hough-Troutman, M. Smiglak, S. Griffin, W.M. Reichert, I. Mirska, J. Jodynis-Liebert, T. Adamska, J. Nawrot, M. Stasiewicz, R.D. Rogers, J. Pernak, New J. Chem. **33**, 26 (2009)
13. F.S. Xiao, L. Wang, C. Yin, K. Lin, Y. Di, J.L. Prof, R.X. Prof, D.S. Su, R. Schlögl, T. Yokoi, T. Tatsumi, ⁋Angew. Chem. **118**, 3162 (2006)
14. J.Y.C. Wu, W.F. Fong, J.X. Zhang, C.H. Leung, H.L. Kwong, M.S. Yang, D. Li, H.Y. Cheung, Eur. J. Pharmacol. **473**, 9 (2003)
15. J.A. Makawana, M.P. Patel, R.G. Patel, Arch. Pharm. **345**, 314 (2012)
16. A.R. Saundane, K. Vijaykumar, A.V. Vaijinath, Bioorg. Med. Chem. Lett. **23**, 1978 (2013)
17. A. Venkatesham, R.S. Rao, K. Nagaiah, J.S. Yadav, G. Roopa-Jones, S.J. Basha, B. Sridhar, A. Addlagatta, Med. Chem. Commun. **3**, 652 (2012)
18. D. Kumar, V.B. Reddy, S. Sharad, U. Dube, S.A. Kapur, Eur. J. Med. Chem. **44**, 3805 (2009)
19. Y.M. Litvinov, A.M. Shestopalov, Synthesis, structure, chemical reactivity, and practical significance of 2-amino-4H-pyrans, in *Advances in Heterocyclic Chemistry*, vol. 103, ed. by A.R. Katritzky (Academic Press, New York, 2011), pp. 175–260
20. S. Paul, S. Ghosh, P. Bhattacharyya, A.R. Das, RSC Adv. **3**, 14254 (2013)
21. S.K. Kundu, J. Mondal, A. Bhaumik, Dalton Trans. **42**, 10515 (2013)
22. S.M. Baghbanian, N. Rezaeiand, H. Tashakorian, Green Chem. **15**, 3446 (2013)
23. R. Ballini, F. Bigi, M.L. Conforti, D.D. Santis, R. Maggi, G. Oppici, G. Sartori, Catal. Today **60**, 305 (2000)
24. J. Albadi, A. Razeghi, A. Mansournezhad, Z. Azarian, J. Nanostruct. Chem. **3**, 85 (2013)
25. S.R. Kale, S.S. Kahandal, A.S. Burange, M.B. Gawande, R.V. Jayaram, Catal. Sci. Technol. **3**, 2050 (2013)
26. R. Ballini, G. Bosica, M.L. Conforti, R. Maggi, A. Mazzacani, P. Righic, G. Sartori, Tetrahedron **57**, 1395 (2001)
27. E. Mosaddegh, Ultrason. Sonochem. **20**, 1436 (2013)
28. D. Kumar, V.B. Reddy, G.B. Mishra, R.K. Rann, M.N. Nadagouda, R.S. Varma, Tetrahedron **63**, 3093 (2007)
29. R. Maggi, R. Balliniand, G. Sartori, Tetrahedron Lett. **45**, 2297 (2004)
30. X.S. Wang, J.X. Zhou, Z.S. Zeng, ARKIVOC **11**, 107 (2006)
31. M.N. Khan, S. Pal, S. Karamthulla, L.H. Choudhury, RSC Adv. **4**, 3732 (2014)
32. T.A. Khan, M. Lal, S. Ali, M.M. Khan, Tetrahedron Lett. **52**, 5327 (2011)
33. W. Kemnitzer, S. Kasibhatla, S. Jiang, H. Zhang, J. Zhao, S. Jia, L. Xu, C. Crogan-Grundy, R. Denis, N. Barriault, L. Vaillancourt, S. Charron, J. Dodd, G. Attardo, D. Labrecque, S. Lamothe, H. Gourdeau, B. Tseng, J. Drewe, S.X. Cai, Bioorg. Med. Chem. Lett. **15**, 4745 (2005)
34. M.M. Heravi, M. Zakeri, N. Mohammadi, Chin. J. Chem. **29**, 1163 (2011)

35. M.N. Elinson, A.I. Ilovaisky, V.M. Merkulova, P.A. Belyakovand, A.O. Chizhov, Tetrahedron **66**, 4043 (2010)
36. T.S. Jin, A.Q. Wang, F. Shi, L.S. Han, L.B. Liu, T.S. Li, Arkivoc **13**, 78 (2006)
37. Y. Peng, G. Song, Catal. Commun. **8**, 111 (2007)
38. A. Shaabani, S. Samadi, Z. Badri, A. Rahmati, Catal. Lett. **104**, 39 (2005)
39. A.R. Moosavi-Zare, M.A. Zolfigol, O. Khaledian, V. Khakyzadeh, M. Darestani Farahani, H.G. Kruge, New J. Chem. **38**, 2342 (2014)
40. S. Sobhani, M. Honarmand, Synlett **24**, 236 (2013)
41. S. Sobhani, M. Honarmand, Appl. Catal. A Gen. **467**, 456 (2013)
42. S. Sobhani, M.S. Ghasemzadeh, M. Honarmand, Catal. Lett. **144**, 1515 (2014)
43. S. Sobhani, M. Honarmand, C. R. Chim. **16**, 279 (2013)
44. J. Aguilo, A. Naeimi, R. Bofill, H.M. Bunz, A. Llobet, L. Escriche, X. Sala, M. Albrech, New J. Chem. **38**, 1980 (2014)
45. A.L. Moreno, D.C. Tejeda, J. Calbo, A. Naeimi, F.A. Bermejo, E. Ortí, E.M. Pérez, Chem. Commun. **50**, 9372 (2014)
46. D. Horak, M. Babic, P. Jendelova, V. Herynek, M. Trchova, Z. Pientka, E. Pollert, M. Hajek, E. Sykova, Bioconjug. Chem. **18**, 635 (2007)
47. L. Fotouhi, M.M. Heravi, A. Fatahi, K. Bakhtiari, Tetrahedron Lett. **48**, 5379 (2007)
48. S. Abdolmohammadi, S. Balalaie, Tetrahedron Lett. **48**, 3299 (2007)
49. A. Khazaei, A. Ranjbaran, F. Abbasi, M. Khazaei, A.R. Moosavi-Zare, RSC Adv. **5**, 13643 (2015)