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1*H*-imidazol-3-ium tricyanomethanide {[HIM]C(CN)$_3$} as a nanostructured molten salt catalyst: application to the synthesis of pyrano[4,3-*b*]pyrans

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Abstract In this work, we have synthesized a novel nanostructured molten salt, ^{1}H-imidazol-3-ium tricyanomethanide {[HIMI]C(CN)$_3$} (1), as an efficient and green protocol-compatible catalyst. This new molten salt has been fully characterized by different analytical techniques, such as FT-IR, ^{1}HNMR, ^{13}CNMR, thermal gravimetric analysis, derivative thermal gravimetric analysis, differential thermal analysis, X-ray diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy. Additionally, the catalytic activity of {[HIMI]C(CN)$_3$} (1, 2 mol%) has been tested in a three-component domino Knoevenagel condensation reaction. A range of structurally diverse aromatic aldehydes (2a–p), malononitrile (3), and 4-hydroxy-6-methyl-2*H*-pyran-2-one (4) are tolerated for the synthesis of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile derivatives (5a–p) under neat conditions at 50 °C. The obtained results have demonstrated that catalyst 1 shows interesting catalytic properties, such

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as clean reaction profile, cost-effectiveness, and green conditions. Importantly, the aforementioned catalyst is thermally stable with a 171 °C melting point not showing any significant loss in catalytic activity after 7 reaction cycles.

Keywords Multicomponent reactions · Knoevenagel condensation · Nanostructured molten salt · Neat conditions · Green chemistry

Introduction

Nowadays, multicomponent reactions (MCRs) have been successfully applied to create highly functionalized and complex molecules via a single procedure [1–11]. This type of reaction have opened up new approaches towards the preparation of combinatorial libraries of varied pharmacologically significant organic molecules and have provided efficient and leading scaffolds towards novel drug discovery. Furthermore, multicomponent reactions involve the one-shot activation of different molecules and bonds providing advantages, such as structural diversity, high selectivity, high atom economy, and green conditions.

The pyrano[4,3-*b*]pyran scaffold, as a non-peptide human immunodeficiency virus inhibitor, shows a noteworthy structural subunit for the discovery of novel drug candidates, such as fused pyran-2-ones. Additionally, the pyrano[4,3-*b*]pyran skeleton has been found in various natural and biologically active products such as davallialactone, arisugacins, pyripyropenes, philigridrins, clavilactone, and territrems [12–14]. The synthesis of pyrano[4,3-b]pyranes is usually performed in a three-component reaction of aldehydes, malononitrile and 4-hydroxy-6-methyl-2*H*-pyran-2-one catalyzed by different systems, such as KF-Al_2O [3, 15] alum [16], *β*-alanine/CaSO [4, 17] eggshell (ES)-supported $Cu(OH)_2$ nanoribbons [18], thiourea dioxide [19], nano-CaO based on eggshell waste [20], electro-catalysis [21], ZnO nanoparticles [22], 4-(succinimido)-1-butane sulfonic acid (SBSA) [23], piperidine [24], heteropolyacid ($H_6P_2W_{18}O_{62}.18H_2O$) [25] and [BBMIm]$(HSO_4)_2$ [26].

Ionic liquids (ILs) and molten salts (MSs) are liquid or solid materials at room temperature fully composed by ions [27–30]. The attention on these compounds as high-tech and green media of the future has rapidly increased due to their high thermal stability, near-zero vapor pressure, tenable properties as regards hydrophobicity, polarity, and solvent miscibility behavior by suitable modification of the cation and the anion. Generally, on account of their uncommon miscibility behavior, ionic liquids present an increased potential to revolutionize reaction technology. The difference between MSs (very corrosive medium, high-melting and highly viscous) and ILs (relatively low viscosity and liquid below 100 °C) is determined by their melting point pattern [31].

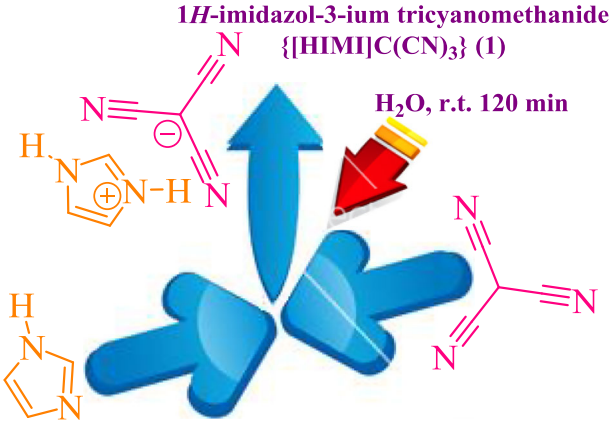
We have previously investigated the design, synthesis, applications, and development of green nanostructured ILs, MSs, and organocatalysts for organic functional group transformations as well as for eco-friendly multicomponent synthesis of biologically heterocyclic compounds [32–47]. As a continuation of these studies, here we report the synthesis of a green mild, efficient, and reusable nanostructured MS catalyst, namely 1H-imidazol-3-ium tricyanomethanide {[HIMI]$C(CN)_3$} (**1**,

Scheme 1) and its catalytic application in a three-component domino Knoevenagel condensation between several structurally diverse aromatic aldehydes, malononitrile, and 4-hydroxy-6-methyl-2*H*-pyran-2-one to prepare 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-*b*]pyran-3 carbonitrile derivatives (**5**) under neat conditions at 50 °C (Scheme 2).

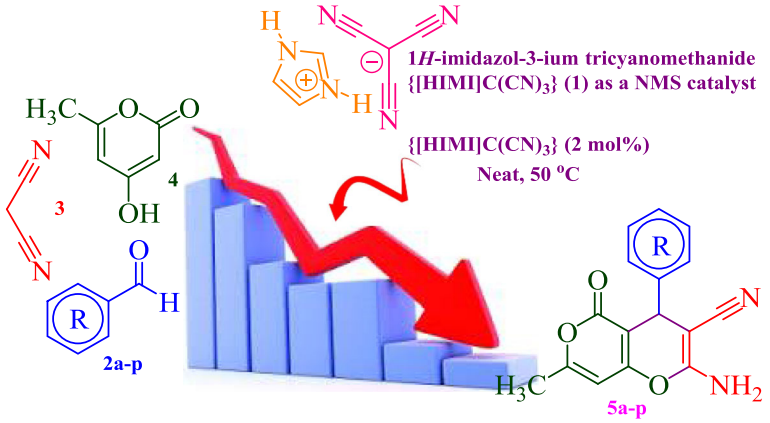
Experimental

Materials and methods

All the materials were purchased from Merck, Fluka, Sigma-Aldrich and Across Organic and were used without any additional purification. All reactions were detected by thin layer chromatography (TLC) on gel F254 plates. Proton-coupled mode NMR (400 or 300 MHz) spectra were recorded on Bruker Avance 400 or Bruker Avance 300 NMR spectrometers, respectively, at 20 °C in DMSO-d_6. Proton-decoupled 13CNMR (100 or 75.5 MHz) spectra were recorded on Bruker Avance 400 and Bruker Avance 300 NMR spectrometers, respectively, at 20 °C in DMSO-d_6; chemical shifts are given in δ (parts per million) and the coupling constants (J) in Hertz. An X-ray diffraction (XRD) pattern of catalyst 1 was attained on a APD 2000, Ital, structure with Cu K_radiation (k = 0.1542 nm) operating at 50 kV and 20 mA in a 2-h range of 10°–70° with step size 0.01° and time step 1.0 s to assess the crystallinity of the catalyst. Fourier transform nfrared (FT-IR) spectra of the samples were recorded on a Perkin–Elmer FT-IR spectrometer 17259 using KBr disks. Thermo-gravimetric analyses were carried out using a Perkin–Elmer TGA apparatus. The scanning electron microscopy (SEM) analyses were prepared with a TESCAN/MIRA with a maximum acceleration voltage of the primary electrons between 10 and 15 kV. The high-resolution transmission electron microscopy (HRTEM) used a HRTEM-200 microscope from JEOL, model JEM-



Scheme 1 Synthesis of 1*H*-imidazol-3-ium tricyanomethanide {[HIMI]C(CN)$_3$} (**1**) as a green, mild, and efficient nanostructured molten salt catalyst



Scheme 2 One-pot three-component synthesis of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano [4,3-*b*]pyran-3-carbonitriles via domino Knoevenagel condensation using {[HIMI]C$(CN)_3$} (**1**) as a new nanostructured molten salt catalyst

2010, working at 200 kV with a LaB6 filament was used for the corresponding studies, with a resolution between layers of 0.14 nm and between points of 0.25 nm. It was equipped with a camera from Gatan, model Orius 831.

General procedure for the synthesis of 1H-imidazol-3-ium tricyanomethanide {[HIMI]C$(CN)_3$} (1)

To an aqueous solution of tricyanomethane (5.0 mmol, 455.0 mg) in deionized water (10 mL) imidazole (5.0 mmol, 340.0 mg) was added and the resulting mixture was stirred at room temperature for 120 min. The solvent was then removed under reduced pressure and the obtained white residue was dried under vacuum at 100 °C during 120 min in a standard glassware oven. The white solid formed was suspended in Et_2O and, after filtration with generous washings with Et_2O, it was dried in vacuo. Then, catalyst 1 was characterized by various techniques, including: FT-IR, ^{1}HNMR, ^{13}CNMR, thermal gravimetric analysis (TGA), derivative thermal gravimetric (DTG) analysis, differential thermal analysis (DTA), X-ray diffraction (XRD), SEM, HRTEM, and melting-point determination.

*1H-imidazol-3-ium tricyanomethanide {[HIMI]C$(CN)_3$} (**1**)*

M.p: 171–173 °C; Yield: (95%, 756.0 mg). FT-IR (KBr): υ 3125, 3023, 2914, 1662, 1549, 1448, 1327, 1100 cm^{-1}. ^{1}HNMR (400 MHz): δ 11.94 (br.s, 2H), 7.62 (s, 1H), 7.00 (s, 2H). ^{13}CNMR (100 MHz): δ 166.4, 135.6, 122.3, 69.6.

General procedure for the synthesis of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile derivatives 5

To a previously prepared mixture in a round-bottom flask of the corresponding aromatic aldehyde (1.0 mmol), 4-hydroxy-6-methyl-2***H***-pyran-2-one (1.0 mmol,

126.0 mg), and malononitrile (1.0 mmol, 66 mg), catalyst 1 (2.0 mol%, 3.2 mg) was added, and the consequent mixture was magnetically stirred under neat conditions at 50 °C. After completion of the reaction, as detected by TLC (n-hexane/ethyl acetate: 5/2), 10 mL of ethyl acetate were added to the mixture, stirred and refluxed for 10 min. The obtained mixture was then washed with water (10 mL) and decanted to separate the NMS catalyst from the reaction mixture. Noticeable, the reaction mixture was soluble in hot ethyl acetate and the NMS catalyst was soluble in water. Then, the organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent, and the crude product was purified via recrystallization from a mixture of ethanol/water: 10/1.

Spectral data for analyzed compounds

Compounds **5b**,[6] **5e**,[6] **5g**,[6] **5h**,[5] **5i**,[5] **5k**,[5] **5l**,[5] **5m**,[13] **5o**,[13] and **5p**[13] are known, and they were characterized by comparison of their physical and spectroscopic data with those described in the literature. Data for the new compounds or those not fully characterized in the literature follow:

*2-Amino-7-methyl-5-oxo-4-phenyl-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**5a**)*

White solid; M.p: 250–252 °C; Yield: (92%, 258 mg). IR (KBr): υ 3400, 3324, 3207, 3084, 2199, 1711, 1674, 1614, 1385, 1261, 1138 cm^{-1}. ^{1}HNMR (400 MHz) δ 7.33 (t, $J = 7.4$ Hz, 2H), 7.25 (t, $J = 9.6$ Hz, 1H), 7.21 (d, $J = 7.2$ Hz, 2H), 7.18 (s, 1H), 6.28 (s, 2H), 4.28 (s, 1H), 2.26 (s, 3H). ^{13}CNMR (100 MHz) δ 162.9, 161.3, 158.1, 158.03, 157.99, 157.95, 143.6, 128.4, 127.5, 127.0, 119.3, 100.7, 97.9, 57.8, 36.2, 19.3.

*2-Amino-4-(4-methoxyphenyl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**5c**)*

White solid; M.p: 212–214 °C; Yield: (90%, 279 mg). IR (KBr): υ 3454, 3313, 3227, 3009, 2185, 1731, 1676, 1646, 1606, 1510, 1380, 1257 cm^{-1}. ^{1}HNMR (400 MHz) δ 7.27 (br.s, 1H), 7.20 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 6.36 (s, 2H), 4.31 (s, 1H), 3.82 (s, 3H), 2.31 (s, 3H). ^{13}CNMR (100 MHz) δ 162.7, 161.3, 158.2, 157.94, 157.90, 157.8, 135.6, 128.6, 119.4, 113.7, 101.0, 97.9, 58.1, 55.0, 35.4, 19.3.

*2-Amino-4-(3-methoxyphenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (**5d**)*

White solid; M.p: 233–235 °C; Yield: (90%, 279 mg). IR (KBr): υ 3411, 3322, 3296, 3185, 3095, 2960, 2208, 1704, 1675, 1644, 1615, 1587, 1383, 1269, 1047 cm^{-1}. ^{1}HNMR (300 MHz) δ 7.26–7.20 (m, 3H), 6.85–6.78 (m, 1H), 6.76–6.72 (m, 2H), 6.28 (d, $J = 0.7$ Hz, 1H), 4.26 (s, 1H), 3.73 (s, 3H), 2.23 (s, 3H). ^{13}CNMR (75 MHz) δ 163.4, 161.8, 159.6, 158.6, 145.6, 130.0, 120.0, 119.7,

114.2, 112.3, 101.1, 98.4, 58.3, 55.4, 36.6, 31.1, 19.8. MS (EI, 70 eV): *m/z* = 282 (M^+–CO, 2%), 184 (100), 156 (25), 141 (20), 127 (30), 114 (34).

*2-Amino-4-(4-cyanophenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (**5f**)*

White solid; M.p: 230–232 °C; Yield: (92%, 281 mg). IR (KBr): υ 3443, 3339, 3230, 3184, 3113, 2226, 2193, 1697, 1669, 1633, 1603, 1584, 1382, 1263, 1139 cm^{-1}. ^{1}HNMR (300 MHz) δ 7.84–7.80 (m, 1H), 7.80–7.75 (m, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.42–7.39 (m, 1H), 7.34 (s, 2H), 6.31 (d, *J* = 0.9 Hz, 1H), 4.43 (s, 1H), 2.23 (s, 3H). ^{13}CNMR (75 MHz) δ 163.9, 161.8, 159.1, 158.6, 149.5, 132.9, 129.2, 119.5, 119.2, 110.3, 100.1, 98.5, 57.3, 36.8, 19.8; MS: m/z = 279 (M^+–CN), 179 (100), 152 (80), 128 (30).

*2-Amino-4-(4-chlorophenyl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**5j**)*

White solid; M.p: 220–222 °C; Yield: 94%, 295 mg). IR (KBr): υ 3383, 3328, 3195, 3098, 2202, 1710, 1674, 1613, 1383, 1261, 1141 cm^{-1}. ^{1}HNMR (400 MHz) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.35 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.38 (s, 2H), 4.41 (s, 1H), 2.32 (s, 3H). ^{13}CNMR (100 MHz) δ 163.1, 161.3, 160.1, 158.2, 142.6, 132.1, 131.5, 129.7, 129.5, 128.3, 119.2, 100.2, 97.9, 57.3, 35.7, 19.3.

*2-Amino-4-(2-fluorophenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (**5n**)*

White solid; M.p: 238–240 °C; Yield: (92%, 274 mg). IR (KBr): υ 3414, 3328, 3305, 3222, 3092, 2198, 1707, 1674, 1644, 1613, 1384, 1260, 1138 cm^{-1}. ^{1}HNMR (300 MHz) δ 7.40–6.96 (m, 6H), 6.30 (d, *J* = 0.9 Hz, 1H), 4.54 (s, 1H), 2.23 (s, 3H). ^{13}CNMR (75 MHz) δ 163.6, 162.6 (d, *J* = 187 Hz), 162.4, 159.1, 158.8, 130.53 (d, *J* = 16 Hz), 130.51 (d, *J* = 12 Hz), 129.6 (d, *J* = 11 Hz), 125.0 (d, *J* = 4 Hz), 119.6, 116.0 (d, *J* = 28 Hz), 99.9, 98.4, 56.9, 31.3, 19.8. MS (EI, 70 eV): *m/z* = 253 (M^+–45, 2%), 172 (100), 145 (90), 121(30).

Results and discussion

Synthesis and characterization of 1H-imidazol-3-ium tricyanomethanide {[HIMI]C(CN)$_3$} (1)

Initially, 1*H*-imidazol-3-ium tricyanomethanide {[HIMI]C(CN)$_3$} (1) was synthesized by the reaction between imidazole and methanetricarbonitrile through a proton transfer mechanism in water for 120 min. The structure of the catalyst (1) was fully characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry, TGA, DTG, DTA, XRD, SEM, and HRTEM analyses.

The FT-IR spectrum of {[HIMI]C(CN)$_3$} (1) (Fig. 1) exhibited a broad peak at 3450 cm^{-1} which can be related to the N–H stretching absorption of the imidazolium moiety. Furthermore, the absorption band at 2079 cm^{-1} is related to the C≡N stretching on the tricyanomethanide counter ion. By comparing the IR absorptions of catalyst 1 and imidazole (Fig. 1), it is clear that not only has the intensity of the band related to the stretching absorption of CN groups decreased but its wavelength has also very slightly shifted to lower values, which could be related to mesomeric effects.

Additionally, we have also studied the structure of {[HIMI]C(CN)$_3$} (**1**) by ^{1}H and ^{13}CNMR spectroscopy (Figs. 2, 3). The experiments were carried out in DMSO-d_6 as solvent and they can be compared with the spectra of the starting materials imidazole and methanetricarbonitrile (see SI, Figs. S1–S4). Regarding the ^{1}HNMR spectrum (Fig. 2), catalyst **1** showed two singlets (7.62 and 7.00 ppm), corresponding to the aromatic protons of the imidazolium ring, and a broad singlet at 11.94 ppm from the most acidic NH protons of the nanostructured molten salt (NMS) catalyst (Fig. 2).

On the other hand, the ^{13}CNMR (100 MHz, DMSO-d_6) spectrum of **1** (Fig. 3) showed two absorption resonances at 166.4 and 69.6 ppm corresponding to the C(CN)$_3$ group. As expected, the absorption resonance peak of the deprotonated carbon had been shifted upfield from the reference value (77.9 ppm) of the starting methanetricarbonitrile (see SI, S2). Finally, two absorption resonances at 135.6 and 122.3 ppm were detected corresponding to the aromatic carbons of the imidazolium ring.

To determine the morphology and size of the nanostructured {[HIMI]C(CN)$_3$} (**1**) catalyst, SEM and HRTEM were studied. This image of the nanostructured {[HIMI]C(CN)$_3$} (**1**) catalyst shows that the average size of these particles is about 63 nm (Fig. 4). HRTEM analysis was completed via selected area electron diffraction (SAED) patterns (Fig. 4b) to study the material's crystalline nature.

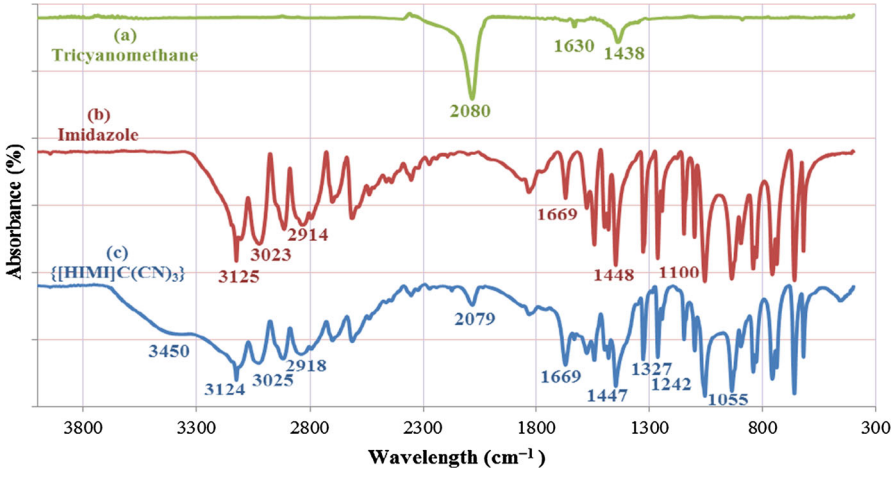


Fig. 1 IR spectrum of tricyanomethane (*a*), imidazole (*b*) and {[HIMI]C(CN)$_3$} (**1**) (*c*)

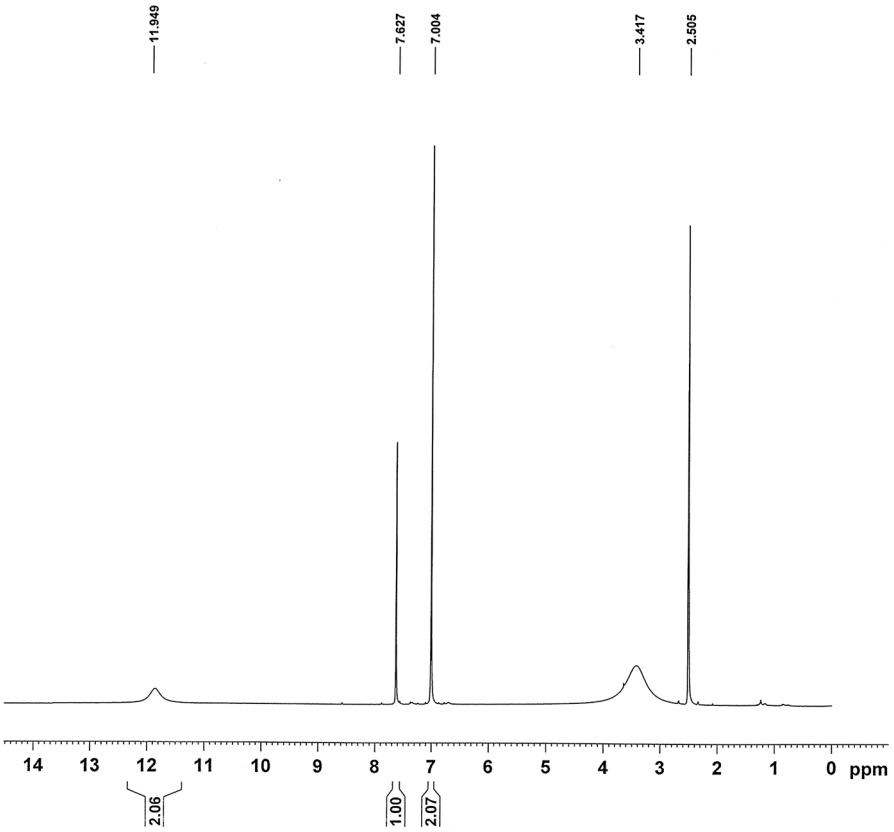


Fig. 2 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of {[HIMI]C(CN)$_3$} (**1**)

The most distinguished SAED ring pattern was confirmed by the XRD results and confirmed the nano-crystalline scale nature of the synthesized NMS catalyst.

Application of {[HIMI]C(CN)$_3$} (1) as a NMS catalyst in the one-pot three-component synthesis of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-b]pyran-3-carbonitriles (5)

To start the study, the condensation of benzaldehyde **2a** with malononitrile **3** and 4-hydroxy-6-methyl-2*H*-pyran-2-one **4** using {[HIMI]C(CN)$_3$} **1** as a NMS catalyst was examined as the reaction model for the optimization (Table 1). First, as depicted in entry 1, we demonstrated that, under neat and catalyst-free conditions, the product was produced in trace amounts at room temperature after 6 h. Interestingly, when increasing the temperature to 50 °C, the reaction preceded smoothly affording (**5a**) in a 43% yield after 6 h. Then, the reaction was performed using 2 mol% of **1** as the catalyst (entry 3), conditions that gratifyingly afforded **5a** in a 92% yield after only 10 min. No improvements were identified in the yield of the reaction by using lower catalyst loadings (entry 5) or different temperatures

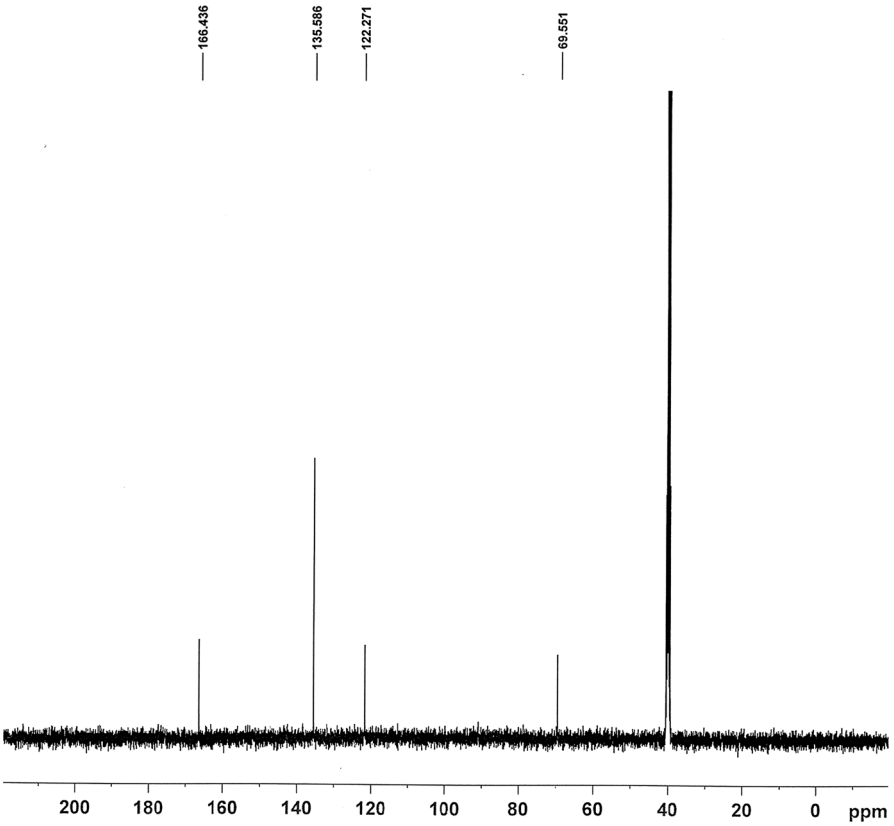


Fig. 3 ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of {[HIMI]C(CN)$_3$} (**1**)

(entries 6 and 7). The reaction was also studied in the presence of different solvents in order to compare the effect of this parameter on the process. Thus, the reaction of benzaldehyde, 4-hydroxy-6-methyl-2*H*-pyran-2-one, and malononitrile in the presence of 2 mol% of NMS and different solvents (H_2O, EtOH, MeCN, EtOAc, and *n*-hexane) was investigated at 50 °C. The obtained results, which are summarized in Table 1, pointed to the neat conditions as the best choice in this process.

After identifying the optimized reaction conditions [**1** (2 mol%), neat conditions at 50 °C], we investigated the scope of the process by performing the reaction of several aldehydes, (**2b**–**p**), with malononitrile and 4-hydroxy-6-methyl-2*H*-pyran-2-one (Table 2). Structurally different aromatic aldehydes with various electron-donating and electron-withdrawing substituents efficiently reacted with 4-hydroxy-6-methyl-2*H*-pyran-2-one and malononitrile under the optimized conditions. As shown in Table 2, a series of aromatic aldehydes underwent electrophilic substitution with malononitrile and 4-hydroxy-6-methyl-2*H*-pyran-2-one to give a wide range of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitriles **5** in good to excellent yields. As shown, the nature and electronic properties of the substituents on the aromatic ring of the aldehydes did not affect the

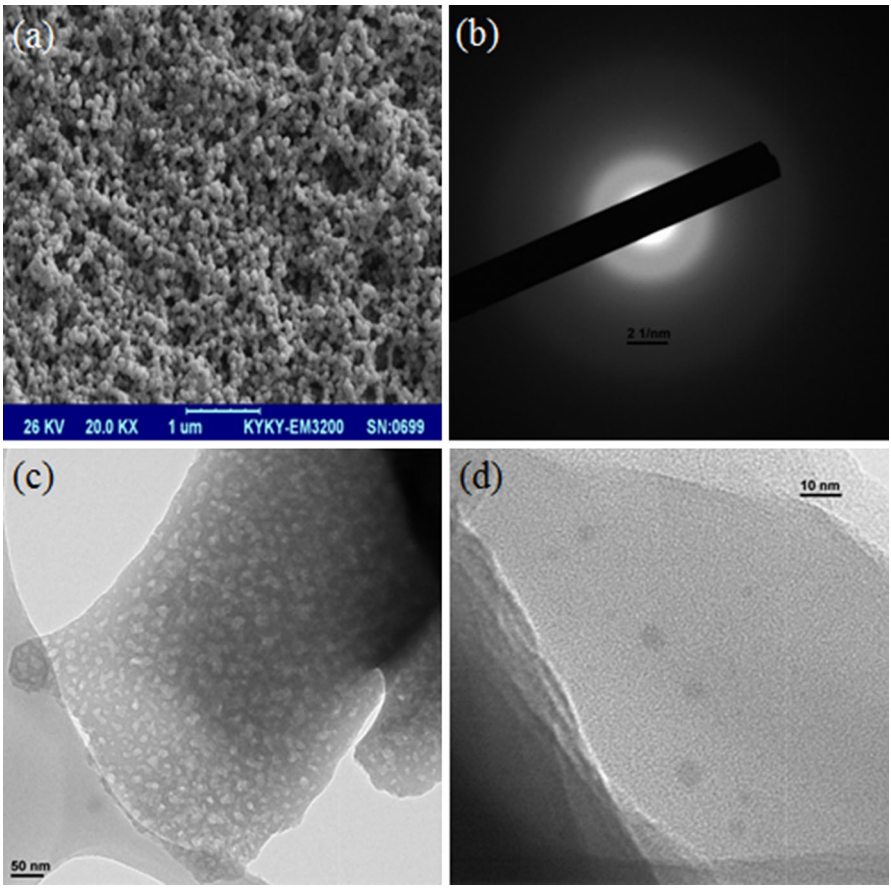


Fig. 4 Scanning electron microscopy (SEM) (**a**), electron diffraction (SAED) patterns (**b**) and transmission electron microscopy (HRTEM) (**c**, **d**) of **1**

reaction yield, although electron-poor aromatic aldehydes reacted faster than electron-rich electrophiles.

A suggested mechanism for the synthesis of the 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitriles via one-pot three-component domino Knoevenagel condensation/6π-electron is shown in Scheme 3 [15–26]. Initially, {[HIMI]C$(CN)_3$} **1**, as a NMS catalyst, activates the carbonyl group of the aromatic aldehyde **2** to give intermediate **6** and tautomerizes malononitrile. The Knoevenagel condensation between intermediates **6** and **7** forms the arylidene malononitrile **8**. Next, 4-hydroxy-6-methyl-2*H*-pyran-2-one **4** performs a conjugate addition over **8** providing adduct **9**, which is further tautomerized by **1** to produce intermediate **10**. Intramolecular cyclization of this compound affords **11**, which suffers a tautomerization process promoted by **1** to provide the corresponding fully aromatized 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitrile **5**.

Table 1 Optimization of reaction conditions

Entry	Solvent	Catalyst loading (mol%)	Temperature (°C)	Time (min)	Isolated yield of **5a** (%)
1	–	–	r.t.	360	Trace
2	–	–	50	360	43
3	**–**	**2**	**50**	**10**	**92**
4	–	1	50	20	87
5	–	0.5	50	60	83
6	–	2	r.t.	60	Trace
7	–	2	70	10	92
8	H_2O	2	50	20	91
9	EtOH	2	50	20	87
10	MeCN	2	50	30	87
11	EtOAc	2	50	60	81
12	*n*-Hexane	2	50	120	63

Reaction conditions: benzaldehyde (2a, 1.0 mmol, 106 mg), malononitrile (3, 1.0 mmol, 66 mg), 4-hydroxy-6-methyl-2*H*-pyran-2-one (4, 1.0 mmol, 126 mg). The optimum reaction conditions (entry 3) are shown in bold

Reusability of {[HIMI]C(CN)$_3$} **1** as a NMS catalyst was confirmed in the condensation of 4-chlorobenzaldehyde **2j**, malononitrile **3**, and 4-hydroxy-6-methyl-2*H*-pyran-2-one **4**. Thus, once the reaction was finished, ethyl acetate was added to the reaction and the resulting mixture was heated. Extraction with water of the hot crude mixture afforded the corresponding product and unreactive starting materials in the organic phase, while the catalyst remained in the aqueous phase. The recovered catalyst could be reused, within the limits of the experimental errors, for seven continuous runs (Fig. 5). Furthermore, the reaction could be scaled up to 10.0 mmol of 4-chlorobenzaldehyde **2j**, malononitrile **3** and 4-hydroxy-6-methyl-2*H*-pyran-2-one **4**, and in the presence of 20 mol% of {[HIMI]C(CN)$_3$} **1** catalyst at 50 °C to afford compound **5j** in a 94% yield after 10 min.

Conclusions

In summary, an efficient, green, and recyclable nanostructured molten salt catalyst, namely 1H-imidazol-3-ium tricyanomethanide {[HIMI]C(CN)$_3$} **1**, was designed, synthesized, and characterized, and its catalytic application was investigated in the one-pot three-component synthesis of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-*b*]pyran 3-carbonitriles via domino Knoevenagel condensation under neat conditions at 50 °C. Compound **1**, as a NMS catalyst, was fully characterized and analyzed by FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry, TGA, DTG, DTA, XRD, SEM, and HRTEM analyses. The proposed mechanism showed that the buffer ability of {[HIMI]C(CN)$_3$} possibly plays an important and dual catalytic role in the defined reaction. Finally, the main advantages of the offered procedure

Table 2 Scope of domino Knoevenagel condensation

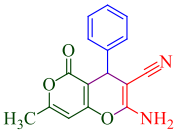
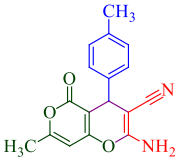
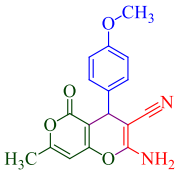
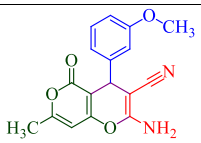
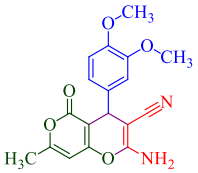
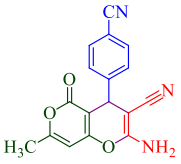
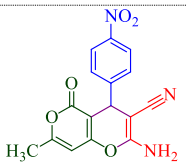
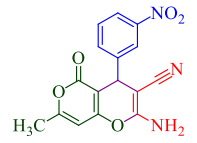
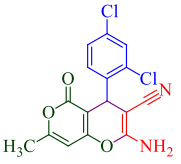
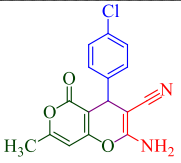
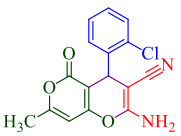
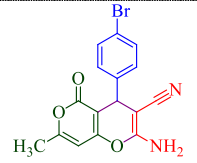
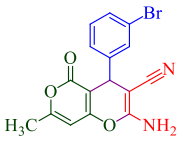
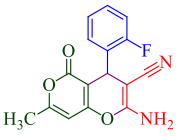
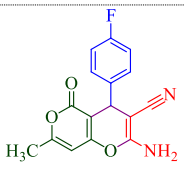
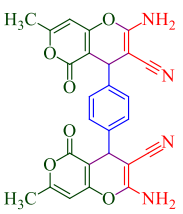
			
5a	**5b**	**5c**	**5d**
10 min., 92%	20 min., 87%	16 min., 90%	15 min., 90%
White solid	White solid	White solid	White solid
M.p: 250-252, [234-236][6]	M.p: 207-209 [224-225][6]	M.p: 212-214, [202-205][6]	M.p: 233-235
			
5e	**5f**	**5g**	**5h**
25 min., 80%	10 min., 92%	12 min., 90%	12 min., 93%
Yellow solid	White solid	Cream solid	White solid
M.p: 144-146 [202-204][6]	M.p: 230-232	M.p: 217-219, [215-218][6]	M.p: 232-234 [238-240][5]
			
5i	**5j**	**5k**	**5l**
12 min., 90%	10 min, 94%	14 min., 91%	11 min., 94%
White solid	White solid	White solid	White solid
M.p: 229-231, [234-235]5	M.p: 220-222, [231-232]5	M.p: 262-264 [270-271]5	M.p: 212-215 [223-225]5

Table 2 continued

			
5m	**5n**	**5o**	**5p**
15 min., 92%	12 min., 92%	11 min., 91%	20 min., 91%
White solid	White solid	White solid	Cream solid
M.p: 258-260 [217-219][13]	238-240	M.p: 231-233 [221-223][13]	M.p: >300 [256-258][13]

Reaction conditions: ArCHO (1.0 mmol), malononitrile (1.0 mmol, 66 mg), 4-hydroxy-6-methyl-2*H*-pyran-2-one (1.0 mmol, 126 mg), **1** (2 mol%, 3.2 mg). Isolated yield. M.p reported in SI unit (°C)

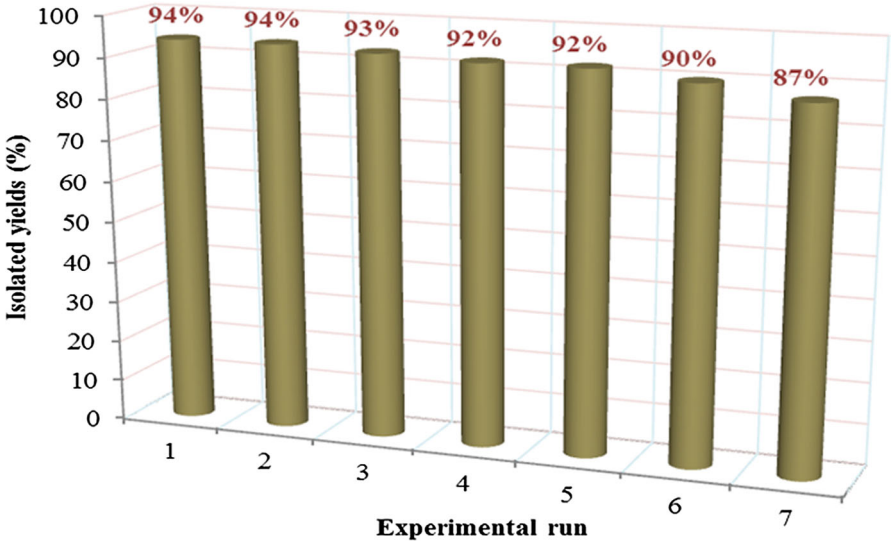
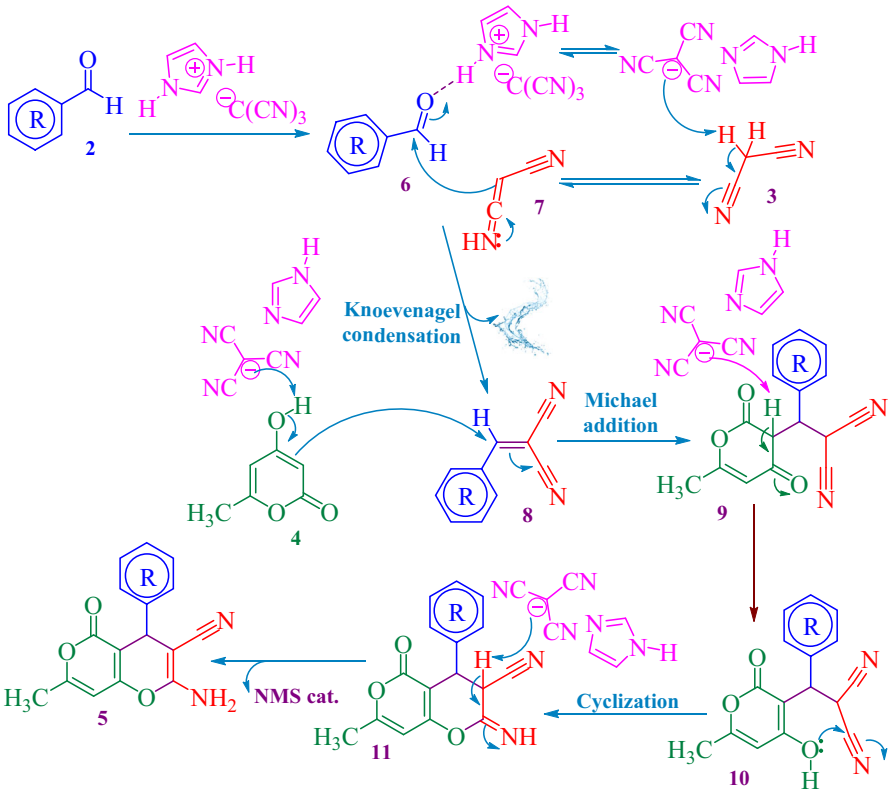


Fig. 5 Reusability study of **1** in the reaction of 4-chlorobenzaldehyde **2j**, malononitrile **3**, and 4-hydroxy-6-methyl-2*H*-pyran-2-one **4**

and/or study are the reasonably low cost, high yield, short reaction time, simple work-up, recoverability, and reusability of the catalyst, and a cleaner reaction profile, being in consequence in close agreement with green chemistry disciplines.



Scheme 3 Proposed mechanism for the synthesis of 2-amino-7-methyl-5-oxo-4-aryl-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitriles **5** by {[HIMI]C(CN)$_3$} **1** as a NMS catalyst

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