1-Methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} as a nano structure and reusable molten salt catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans *via* tandem Knoevenagel-Michael cyclocondensation and 3,4-dihydropyrano[*c*]chromene derivatives

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Abstract: An expeditious, experimentally simple and rapid 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} nano molten salt (NMS) catalyzed tandem Knoevenagel-Michael cyclocondensation procedure for the synthesis of tetrahydrobenzo[*b*]pyrans was described *via* reaction between dimedone, aromatic aldehyde and malononitrile under solvent-free conditions at room temperature. Furthermore, 3,4-dihydropyrano[*c*]chromene derivatives through the condensation of 4-hydroxycoumarin, aromatic aldehyde and malononitrile were synthesized by a catalytic amount of {[HMIM]C(CN)₃} NMS under the same condition.

Keywords: 1-Methylimidazolium tricyanomethanide {[HMIM]C(CN)₃}, Nano molten salt (NMS), Tetrahydrobenzo[*b*]pyrans, 3,4-Dihydropyrano[*c*]chromene, Solvent-free.

1. Introduction

By green chemistry principal issues in both educational and industrial investigation in the 21st century, the improvement of ecofriendly benign and clean synthetic processes nowadays has become the purpose in organic synthesis. Some organic solvents are harmful and their use should be limited as far as possible or even prohibited totally [1]. Ionic liquids (ILs) or molten salts (MSs) are generally known as liquid electrolytes and hydro-tropes composed completely of ions [2]. Most recently, the melting point criterion has been offered to distinguish between molten salts “highly viscous, high-melting and very corrosive medium” and ionic liquids “liquid below 100 °C and relatively low viscosity” [3]. However, MSs or ILs are better defined as liquid compounds in that they show ionic covalent crystalline structures. “A considerable benefit of the molten salt medium, though, is that the product may be separated using decantation or simple distillation” in contrast to the reaction work-up in conventional organic solvents which cannot be separated so [4]. Disregarding the polarization process used, molecular dynamics simulations of molten salts in which polarization effects are involved have exposed that the liquids become more mobile [5]. Molten salts are an attractive class of liquids owing to their unique ionic interactions and their varied number of scientific usages [6]. The explanation of molten salts is based on columbic interaction, steric hindrances and polarization phenomenon. Despite the simplicity, there are still several problems on the structure and the dynamics of high temperature MSs [7].

Multi-component reactions (MCRs) are appeared as an efficient and influential tool in modern synthetic organic chemistry to achieve desirable molecular diversity. MCRs allow chemists to perform reaction of numerous new bonds in a one-pot reaction. Strecker was the first chemist that applied MCRs for the synthesis of amino acids [8]. In the past decade, considerable improvements in MCRs have been made and great efforts are repeatedly being made to improve novel MCRs [9]. Two such multi-component reactions are the synthesis of

tetrahydrobenzo[*b*]pyrans *via* tandem Knoevenagel-Michael cyclocondensation and 3,4-dihydropyrano[*c*]chromene derivatives. 4*H*-Pyran nucleus create structural types of a wide number of natural products [10]. The tetrahydrobenzo[*b*]pyran ring is mostly considered as a structural component of compounds having biological activity as anticancer, spasmolytic, anticoagulant, anti-anaphylactic agents [11]. Also, they can be used as cognitive enhancers for the treatment of neurodegenerative illness including Huntington's sickness, amyotrophic lateral sclerosis, Parkinson's illness, Alzheimer's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of myoclonus and schizophrenia [12]. Various reagents such as KF-basic alumina under ultrasound irradiation [13], hexadecyltrimethylammonium bromide (HTMAB) [14], electrolysis [15], tetramethylammonium hydroxide (TMAH) [16] and amino-functionalized ionic liquid [17] were used to catalyze these reactions.

Dihydropyrano[*c*]chromenes and their corresponding derivatives are of significant importance as they have a broad range of biological properties such as anticancer [18], cytotoxicity [19], anticoagulant [20], diuretic, analgesic, myorelaxant [21], anti-tumor [22] and anti-HIV [23]. Numerous methods have been reported for the synthesis of 3,4-dihydropyrano[*c*]chromenes by several catalysts such as DBU [24], nanostructured ZnO [25], tetrabutylammonium bromide [26], pyridine [27] and morpholine [28].

Most recently, the first nano ionic liquid and molten salts were reported by our research group and they were employed as nano catalysts in a worthy variety of organic reactions [29]. Subsequently, to overcome those problems and in our continuous investigation in the improvement of "NOSE" (nanoparticle-catalyzed organic synthesis enhancement) chemistry [30], we herein study an appropriate process for 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} as a green effective nano molten salt (NMS) catalyzed the synthesis of tetrahydrobenzo[*b*]pyrans *via* tandem Knoevenagel-Michael

cyclocondensation and 3,4-dihydropyrano[c]chromene derivatives under solvent-free conditions (Scheme 1).

>Scheme 1<

2. Experimental

General procedure for the preparation of NMS catalyst: 1-methylimidazolium tricyanomethanide

The nano structure molten salt {[HMIM]C(CN)₃} as a catalyst was synthesized according to our previously reported procedure [29a]. 1-Methylimidazole (3 mmol: 0.246 g) was added to 5 mL of tricyanomethane aqueous solution (3 mmol: 0.273 g) and stirred at room temperature for 60 minutes. Consequently the solvent was removed through distillation under reduced pressure; the white residue was dried under vacuum at 100 °C for 3 h. A pale pink solid prepared which was filtered, washed with diethyl ether three times, and then dried under vacuum (a pale pink solid was insoluble in diethyl ether) and was characterized by FT-IR, ¹H NMR, ¹³C NMR, mass, TG, DTG, XRD, SEM, TEM analysis and melting-point determination. Nano structure molten salt {[HMIM]C(CN)₃} as a catalyst was achieved in high purity and then the physical data of these known NMS was found to be identical with: M.p: >300 °C; Yield: 96% (0.498 g); Spectral data: IR (KBr): ν 3417, 2925, 2170, 2081, 1631, 1574, 1455 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.63 (s, 3H, —CH₃), 7.00 (s, 2H, —CH); 7.63 (s, 1H,—CH), 11.95 (brs, 1H, —NH); ¹³CNMR (100 MHz, DMSO-*d*₆): δ 46.4, 67.2, 74.8, 119.8, 134.9, 160.2; MS: *m/z* = 173 [M]⁺.

General procedure for the synthesis of tetrahydrobenzo[b]pyrans derivatives

{[HMIM]C(CN)₃} as a nano structure molten salt catalyst (0.5 mol%) was added to a mixture of several aromatic aldehydes (1 mmol), malononitrile (1 mmol) and dimedone (1 mmol) in a round bottom flask, and the resultant mixture was stirred magnetically

under solvent-free conditions at room temperature. After completion of the reaction, as monitored by TLC *n*-hexane/ethyl acetate (5:2), ethyl acetate (10 mL) was added to the reaction mixture, stirred and refluxed for 3 min, and then was washed with water (10 mL) and decanted to separate catalyst from the other materials (the reaction mixture was soluble in hot ethyl acetate and nano structure molten salt catalyst was soluble in water). The aqueous layer was decanted and the catalyst was separated after removing water. The remained catalyst was used for the alternative reaction. The solvent of organic layer was evaporated and the crude product was purified by recrystallization in ethanol/water (10:1). In the present work, nano structure molten salt catalyst was recycled and reused for four times without important loss of its catalytic activity.

General procedure for the synthesis of 3,4-dihydropyrano[c]chromene derivatives

{[HMIM]C(CN)₃} as a NMS catalyst (0.5 mol%) was added to a mixture of several aromatic aldehydes (1 mmol), malononitrile (1 mmol) and 4-hydroxycoumain (1 mmol) in a round bottom flask, and the subsequent mixture was stirred magnetically under solvent-free conditions at room temperature. After completion of the reaction, as checked by TLC *n*-hexane/ethyl acetate (5:3), ethyl acetate (10 mL) was added to the reaction mixture, stirred and refluxed for 3 min, and then was washed with water (10 mL) and decanted to separate catalyst from the other materials (the reaction mixture was soluble in hot ethyl acetate and nano structure molten salt catalyst was soluble in water). The aqueous layer was decanted and the catalyst was separated after removing water. The remained catalyst was used for the alternative reaction. The solvent of organic layer was evaporated and the crude product was purified by recrystallization in ethanol/water (10:1). In the present work, NMS catalyst was recycled and reused for four times without important loss of its catalytic activity.

Spectral data analysis for compounds

2-Amino-4-(3-ethoxy-4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 6): White solid; M.p: 218-220 °C; Yield: 95%; IR (KBr): ν 3473, 3382, 3354, 3215, 2195, 1687, 1604, 1372 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6): δ_{ppm} 1.02 (s, 6H, —CH₃), 2.12 (d, 2H, J = 7.1 Hz, —CH₂), 2.27 (d, 2H, J = 9.9 Hz, —CH₂), 2.51 (t, 3H, J = 5.0 Hz, —CH₃), 3.34 (q, 2H, J = 8.0 Hz, —CH₂), 4.28 (s, 2H, —CH aliphatic and —OH), 5.17 (s, 2H, —NH₂), 7.15 (s, 1H, ArH), 7.36 (d, 1H, J = 5.4 Hz, ArH), 7.75 (d, 1H, J = 5.6 Hz, ArH); ^{13}C NMR (75 MHz, DMSO- d_6): δ_{ppm} 27.0, 28.3, 31.9, 35.8, 49.9, 57.1, 109.5, 111.7, 118.8, 128.4, 132.5, 150.3, 158.5, 163.1, 195.8.

2-Amino-4-(2-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 9): Yellow solid; M.p: 247-249 °C; Yield: 92%; IR (KBr): ν 3439, 3386, 2955, 2207, 1659, 1627, 1383 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ_{ppm} 0.96 (s, 3H, —CH₃), 1.04 (s, 3H, —CH₃), 2.15 (d, 2H, J = 8.0 Hz, —CH₂), 2.28 (d, 2H, J = 8.2 Hz, —CH₂), 2.53 (s, 1H, —OH), 4.22 (s, 1H, —CH aliphatic), 7.13 (t, 1H, J = 6.2 Hz, ArH), 7.17 (s, 2H, —NH₂), 7.27 (d, 2H, J = 8.0 Hz, ArH), 7.36 (t, 1H, J = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ_{ppm} 26.8, 28.2, 31.8, 35.3, 49.9, 57.6, 112.0, 119.4, 125.9, 126.6, 127.0, 130.3, 132.9, 147.2, 158.4, 158.5, 195.7.

2-Amino-4-(2-hydroxy-3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 10): Orange solid; M.p: 181-183 °C; Yield: 92%; IR (KBr): ν 3562, 3391, 3348, 2954, 2290, 1590, 1482 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ_{ppm} 3.12 (s, 3H, —CH₃), 3.40 (s, 3H, —CH₃), 3.47 (s, 3H, —CH₃), 3.56 (s, 2H, —NH₂), 3.66 (s, 1H, —OH), 3.79 (d, 2H, J = 4.4 Hz, —CH₂), 3.90 (d, 2H, J = 4.0 Hz, —CH₂), 5.18 (s, 1H, —CH aliphatic), 6.53 (t, 1H, J = 7.8 Hz, ArH), 6.73 (d, 1H, J = 8.4 Hz, ArH), 6.84 (d, 1H, J = 4.8 Hz, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ_{ppm} 27.9, 43.0, 55.3, 60.3, 61.9, 62.0, 72.7, 123.3, 138.3, 147.9, 150.9, 158.5, 164.4, 166.5, 168.5, 182.1, 183.2, 183.3, 196.1.

2-Amino-4-(2,5-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 11): Cream solid; M.p: 181-183 °C; Yield: 95%; IR (KBr): ν 3391, 3334, 3216, 2951, 2193, 1682, 1650, 1499, 1374 cm^{-1} ; ^1H NMR (300 MHz, DMSO- d_6): δ_{ppm} 1.03 (s, 6H, —CH₃), 2.08 (d, 2H, J = 7.2 Hz, —CH₂), 2.27 (d, 2H, J = 7.1 Hz, —CH₂), 3.69 (s, 6H, —CH₃), 4.42 (s, 1H, —CH aliphatic), 5.17 (s, 2H, —NH₂), 6.50 (s, 1H, ArH), 6.73 (d, 1H, J = 5.8 Hz, ArH), 6.89 (d, 1H, J = 6.0 Hz, ArH); ^{13}C NMR (75 MHz, DMSO- d_6): δ_{ppm} 26.5, 28.7, 31.8, 50.0, 55.2, 56.3, 57.2, 111.5, 111.8, 112.6, 114.8, 119.8, 133.5, 151.0, 153.1, 158.9, 163.2, 195.6.

4,4'-(1,4-Phenylene)bis(2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile) (Table 3, entry 13): White solid; M.p: 273-275 °C; Yield: 94%; IR (KBr): ν 3452, 3332, 3260, 3190, 2964, 2198, 1683, 1663, 1363 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ_{ppm} 0.99 (s, 6H, —CH₃), 1.04 (s, 6H, —CH₃), 2.19 (d, 4H, J = 8.0 Hz, —CH₂), 2.26 (d, 4H, J = 8.0 Hz, —CH₂), 4.14 (s, 2H, —CH aliphatic), 6.97 (s, 4H, —NH₂), 7.04 (s, 4H, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ_{ppm} 27.2, 28.2, 31.8, 34.9, 49.9, 58.3, 112.7, 112.8, 119.7, 126.9, 142.8, 158.4, 158.5, 162.7, 195.8.

2-Amino-7,7-dimethyl-5-oxo-4-(pyridin-4-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 14): Brown solid; M.p: 182-184 °C; Yield: 92%; IR (KBr): ν 3419, 3324, 3182, 2958, 2189, 1687, 1601, 1370 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ_{ppm} 0.95 (s, 3H, —CH₃), 1.04 (s, 3H, —CH₃), 2.13 (d, 2H, J = 8.0 Hz, —CH₂), 2.27 (d, 2H, J = 8.0 Hz, —CH₂), 4.18 (s, 1H, —CH aliphatic), 7.07 (s, 2H, —NH₂), 7.13 (d, 1H, J = 7.6 Hz, ArH), 7.50 (d, 1H, J = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ_{ppm} 26.8, 28.3, 31.8, 35.1, 49.9, 55.9, 57.6, 112.2, 119.5, 119.6, 129.5, 131.2, 144.1, 158.3, 158.4, 162.6, 195.7.

2-Amino-4-(2,4-dihydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 18): Orange solid; M.p: 249-251 °C; Yield: 92%; IR (KBr): ν 3456, 3399, 3368, 3244, 2957, 2199, 1637, 1612, 1572, 1377 cm^{-1} ; ^1H NMR (300

MHz, DMSO-*d*₆): δ_{ppm} 0.90 (s, 6H, —CH₃), 1.06 (d, 2H, *J* = 7.1 Hz, —CH₂), 2.15 (d, 2H, *J* = 8.6 Hz, —CH₂), 4.98 (s, 1H, —CH aliphatic), 5.98 (s, 2H, —OH), 6.18 (s, 2H, —NH₂), 6.28 (s, 1H, ArH), 6.38 (d, 1H, *J* = 5.6 Hz, ArH), 6.66 (d, 1H, *J* = 5.4 Hz, ArH); ¹³C NMR (75 MHz, DMSO-*d*₆): δ_{ppm} 27.0, 28.3, 31.9, 35.8, 49.9, 57.1, 118.8, 118.9, 122.6, 124.8, 128.9, 132.5, 133.2, 148.8, 152.3, 153.9, 158.0, 195.8.

2-Amino-4-(3,4-dihydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 19): White solid; M.p: 241-243 °C; Yield: 92%; IR (KBr): ν 3468, 3408, 3319, 3235, 2955, 2202, 1677, 1599, 1358 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆): δ_{ppm} 1.02 (s, 6H, —CH₃), 2.10 (d, 1H, *J* = 7.2 Hz, —CH₂), 2.26 (d, 1H, *J* = 7.1 Hz, —CH₂), 2.49 (d, 1H, *J* = 4.4 Hz, —CH₂), 3.35 (d, 1H, *J* = 4.8 Hz, —CH₂), 3.96 (s, 1H, —CH aliphatic), 6.38 (d, 1H, *J* = 5.4 Hz, ArH), 6.51 (s, 1H, ArH), 6.61 (d, 1H, *J* = 5.4 Hz, ArH), 6.91 (s, 2H, —NH₂), 8.72 (s, 1H, —OH), 8.83 (s, 1H, —OH); ¹³C NMR (75 MHz, DMSO-*d*₆): δ_{ppm} 26.8, 28.5, 31.8, 34.8, 50.1, 58.8, 113.3, 114.6, 115.3, 117.9, 120.0, 135.8, 143.9, 144.9, 158.4, 161.9, 195.7.

*2-Amino-4-(2-hydroxy-3-methoxyphenyl)-5-oxo-4H,5H-pyrano[3,2-*c*]chromene-3-carbonitrile* (Table 6, entry 11): Orange solid; M.p: 231-233 °C; Yield: 93%; IR (KBr): ν 3439, 3320, 3195, 3074, 2946, 2203, 1712, 1663, 1509, 1272 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 3.94 (s, 3H, —CH₃), 4.89 (s, 1H, —CH aliphatic), 6.56 (d, 1H, *J* = 7.6 Hz, ArH), 6.61 (s, 1H, —OH), 6.93 (d, 1H, *J* = 6.47 Hz, ArH), 7.12 (t, 3H, *J* = 7.6 Hz, ArH), 7.22 (d, 1H, *J* = 3.2 Hz, ArH), 4.41 (s, 4H, —NH₂), 7.83 (d, 1H, *J* = 6.0 Hz, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ_{ppm} 55.5, 72.7, 109.9, 115.1, 115.2, 115.5, 117.1, 121.5, 121.9, 124.4, 125.2, 129.6, 129.7, 129.8, 132.1, 148.4, 153.2, 163.2, 172.1, 174.0.

*2-Amino-4-(2,4-dihydroxyphenyl)-5-oxo-4H,5H-pyrano[3,2-*c*]chromene-3-carbonitrile* (Table 6, entry 19): White solid; M.p: 208-210 °C; Yield: 90%; IR (KBr): ν 3419, 3388, 3236, 2199, 1670, 1629, 1599, 1509, 1399 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 5.19

(s, 1H, —OH), 5.29 (s, 1H, —OH), 6.06 (s, 1H, —CH aliphatic), 6.33 (t, 1H, $J = 8.8$ Hz, ArH), 6.72 (d, 2H, $J = 8.4$ Hz, ArH), 7.01 (s, 1H, ArH), 7.12 (s, 2H, —NH₂), 7.36 (d, 2H, $J = 8.2$ Hz, ArH), 7.80 (t, 1H, $J = 8.4$ Hz, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ_{ppm} 27.1, 84.5, 105.4, 106.2, 106.9, 107.7, 130.4, 150.0, 164.7, 165.5, 166.2, 167.2, 173.2, 179.6, 179.7, 179.9, 180.9, 182.0.

*2-Amino-4-(3,4-dihydroxyphenyl)-5-oxo-4H,5H-pyrano[3,2-*c*]chromene-3-carbonitrile* (Table 6, entry 20): White solid; M.p: 296-298 °C; Yield: 93%; IR (KBr): ν 3369, 3282, 3245, 3170, 2201, 1706, 1673, 1605, 1377 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 4.25 (s, 1H, —CH aliphatic), 5.07 (s, 1H, —NH₂), 5.52 (d, 1H, $J = 8.0$ Hz, ArH), 6.66 (t, 1H, $J = 7.2$ Hz, ArH), 7.33 (s, 1H, ArH), 7.51 (d, 2H, $J = 7.6$ Hz, ArH), 7.73 (t, 1H, $J = 7.6$ Hz, ArH), 7.91 (d, 1H, $J = 7.6$ Hz, ArH), 8.84 (s, 1H, —OH), 8.91 (s, 1H, —OH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ_{ppm} 36.2, 104.0, 104.6, 112.9, 114.7, 114.8, 115.4, 115.5, 116.5, 118.4, 119.3, 122.3, 124.7, 132.8, 134.3, 152.0, 152.8, 157.8, 159.5.

3. Results and discussion

*Application of {[HMIM]C(CN)₃} as a NMS catalyst in the tandem Knoevenagel-Michael cyclocondensation synthesis of tetrahydrobenzo[*b*]pyran derivatives.*

Knowledge-based design and synthesis of task specific ionic liquids and molten salts [29], solid acids [31], inorganic acidic salts [32] and biological based solid acids [33] are our main purpose because these catalytic systems play a dominant role in the organic functional groups transformations. With this aim, 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} as a green effective nano molten salt (NMS) was synthesized and applied as a catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans via tandem Knoevenagel-Michael cyclocondensation and 3,4-dihydropyrano[*c*]chromene derivatives under solvent-free conditions

Firstly, to optimize the reaction conditions, the condensation reaction of 2,5-

dimethoxybenzaldehyde, malononitrile and dimedone were selected as a typical reaction and different amounts of {[HMIM]C(CN)₃} as a NMS catalyst at range of 25–100 °C under solvent-free conditions (Table 1). As shown in Table 1, the best results were attained when the reaction was performed using 0.5 mol% of MNPs catalyst at room temperature (Table 1, entry 3). No improvement was identified in the yield of reaction through increasing the amount of the NMS catalyst and temperature (Table 1, entries 4–11). Table 1 clearly displays that in the absence of NMS catalyst, the product was synthesized with low yield (Table 1, entries 1 and 2).

>Table 1<

To compare the result of the solution with that of solvent-free conditions, a mixture of 2,5-dimethoxybenzaldehyde, malononitrile and dimedone as a model reaction, in the presence of 0.5 mol% of {[HMIM]C(CN)₃} as a NMS catalyst in different solvents was considered at room temperature. The results are presented in Table 2. As it can be seen in Table 2, solvent-free condition was the best one in this reaction.

>Table 2<

After identifying the optimized reaction conditions, the research was followed by performing the reaction between aromatic aldehydes with malononitrile and dimedone. To show the general applicability of this procedure, numerous aldehydes were efficiently reacted with malononitrile and dimedone in the similar conditions. These results encouraged us to investigate the scope and the overview of this process for several aldehydes under optimized conditions. As revealed in Table 3, a series of aromatic aldehydes underwent electrophilic substitution reaction with malononitrile and dimedone to provide a different range of substituted tetrahydrobenzo[*b*]pyrans in good to excellent yields. The nature and electronic properties of the substituents on the aromatic ring effect the alteration rate, and aromatic aldehydes having electron-withdrawing groups on the

aromatic ring react faster than electron-donating groups.

>Table 3<

A probable mechanism for the formation of the tetrahydrobenzo[*b*]pyran (**4**) is defined in Scheme 2 [34c]. Initially, {[HMIM]C(CN)₃} as a NMS catalyst activates the carbonyl group of the aromatic aldehyde to give intermediate (**7**) and malononitrile (**5**) tautomerized to (**8**). The Knoevenagel condensation of intermediate (**7**) and (**8**) was occurred to form the arylidene malononitrile (**10**). Subsequently, dimedone (**3**) tautomerized to (**9**) which tolerates nucleophilic attack to (**10**) and provides the Michael adduct (**11**). The Michael adduct (**11**) tautomerizes by {[HMIM]C(CN)₃} as a NMS catalyst to create intermediate (**12**) which cyclizes to offer compound (**13**) and then tautomerized to provide the fully aromatized tetrahydrobenzo[*b*]pyran (**4**).

>Scheme 2<

Moreover, reusability of the NMS catalyst was confirmed *via* the condensation of 2,5-dimethoxybenzaldehyde, malononitrile and dimedone. At the end of the reaction, ethyl acetate was added to the reaction mixture and heated to extract product from remained starting materials. This solution was washed with water to separate catalyst from other materials (the product is soluble in hot ethyl acetate and NMS catalyst is soluble in water). The aqueous layer was decanted, separated and applied for further reaction after removing water. It was confirmed that the catalytic activity of the catalyst was restored within the limits of the experimental errors for four continuous runs (Fig. 1).

>Fig. 1<

*Application of {[HMIM]C(CN)₃} as a NMS catalyst in synthesis of 3,4-dihydropyrano[*c*]chromene derivatives.*

After the synthesis of tetrahydrobenzo[*b*]pyran derivatives, in the additional work for the synthesis of 3,4-dihydropyrano[*c*]chromene derivatives, to optimize the reaction

conditions, the condensation reaction of 2,5-dimethoxybenzaldehyde, malononitrile and 4-hydroxycoumarin was chosen as a model and different amounts of {[HMIM]C(CN)₃} as a NMS catalyst at range of 25–100 °C under solvent-free conditions were studied (Table 4). As shown in Table 4, the best results were achieved when the reaction was attained in the presence of 0.5 mol% of {[HMIM]C(CN)₃} as a NMS catalyst at room temperature (Table 4, entry 3). No improvement was identified in the yield of reaction *via* increasing the amount of the NMS catalyst and temperature (Table 4, entries 4-11).

>Table 4<

To compare the proficiency of the solution with solvent-free conditions, a mixture of 2,5-dimethoxybenzaldehyde, malononitrile and 4-hydroxycoumarin as typical reaction, in the presence of 0.5 mol% of NMS as a catalyst in numerous solvents such as H₂O, C₂H₅OH, CH₃CN, CH₃CO₂Et and CH₂Cl₂ was studied at room temperature. The results are summarized in Table 5. As it can be realized in Table 5, solvent-free condition was the best conditions in this reaction.

>Table 5<

After optimization of the reaction conditions, to study the efficacy and the scope of the offered process, many 3,4-dihydropyrano[*c*]chromene derivatives were synthesized *via* the one-pot three-component condensation reaction between aromatic aldehydes with malononitrile and 4-hydroxycoumarin in the presence of catalytic amounts of {[HMIM]C(CN)₃} as a NMS under solvent-free reaction conditions. The results are displayed in Table 6. The effect of substituents on the aromatic ring was assessed strong in terms of yields under these reaction conditions. Both classes of aromatic aldehydes including electron-releasing and electron-withdrawing substituents on their aromatic ring gained the related products in high to excellent yields in short reaction time. The reaction time of

aromatic aldehydes having electron withdrawing groups was rather faster than electron donating groups.

>Table 6<

A possible mechanism for the creation of the 3,4-dihydropyrano[*c*]chromene (**6**) was defined in Scheme 3 [35e]. Firstly, {[HMIM]C(CN)₃} as a NMS catalyst activates the carbonyl group of the aromatic aldehyde to give intermediate (**7**) and malononitrile (**5**) tautomerized to (**8**). The Knoevenagel condensation of intermediate (**7**) and (**8**) was occurred to form the arylidene malononitrile (**10**). Then, 4-hydroxycoumarin (**5**) tolerates nucleophilic attack to (**10**) and affords the Michael adduct (**14**). The Michael adduct (**14**) tautomerizes using {[HMIM]C(CN)₃} as a NMS catalyst to create intermediate (**15**) which cyclizes to offer compound (**16**) and then tautomerized to afford the fully aromatized 3,4-dihydropyrano[*c*]chromene (**6**).

>Scheme 3<

Furthermore, reusability of the NMS catalyst was confirmed by the condensation of 2,5-dimethoxybenzaldehyde, malononitrile and 4-hydroxycoumarin. At the end of the reaction, ethyl acetate was added to the reaction mixture and heated to extract product from remained starting materials. This solution was washed with water to separate catalyst from other materials (the product is soluble in hot ethyl acetate and NMS catalyst is soluble in water). The aqueous layer was decanted, separated and used for additional reaction after removing water. It has been known that the catalytic activity of the catalyst was restored within the limits of the experimental errors for four continuous runs (Fig. 2).

>Fig. 2<

4. Conclusion

In conclusion, a green, reusable and ecofriendly NMS catalyst namely 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} was used and studied in the

synthesis of tetrahydrobenzo[*b*]pyrans *via* tandem Knoevenagel-Michael cyclocondensation by three-component condensation reaction of numerous aromatic aldehydes, malononitrile and dimedone under solvent-free conditions at room temperature. Afterwards, 3,4-dihydropyrano[*c*]chromene derivatives were also synthesized *via* three-component condensation reaction of numerous aromatic aldehydes, malononitrile and 4-hydroxycoumain under similar reaction conditions. The offered mechanisms revealed that the buffer ability of nano molten salt, possibly plays an important dual catalytic role in the described reactions. finally, significant advantages of the offered methodology and study are reasonably cleaner reaction profile, simple work up, short reaction time, high yield, recyclability and reusability of the NMS catalyst which is in close agreement with the green chemistry disciplines.

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References

- [1] M. Eissen, J.O. Metzger, E. Schmidt, U. Schneidewind, 10 Years after rio—concepts on the contribution of chemistry to a sustainable development, *Angew. Chem. Int. Ed. Engl.*, 41 (2002) 414-436.
- [2] A.F.M. Cláudio, M.C. Neves, K. Shimizu, J.N.C. Lopes, M.G. Freire, J.A.P. Coutinho, The magic of aqueous solutions of ionic liquids: Ionic liquids as a powerful class of catanionic hydrotropes, *Green Chem.*, 17 (1015) 3948-3963.
- [3] P. Wasserscheid, W. Keim, Ionic liquids-new " solutions" for transition metal catalysis, *Angew. Chem., Int. Ed.*, 39 (2000) 3773-3789.

- [4] G.W. Parshall, Catalysis in molten salt media, *J. Am. Chem. Soc.*, 94 (1972) 8716-8719.
- [5] (a) P.A. Madden, M. Wilson. Covalent effects in ionic liquids, *J. Phys. Condens. Matter.*, 12 (2000) A95-A108; (b) L.J.A. Siqueira, S. Urahata, M.C.C. Ribeiro, Molecular dynamics simulation of molten sodium chlorate, *J. Chem. Phys.*, 119 (2003) 8002-8012.
- [6] J.S. Wilkes, G. Mamantov, R. Marassi, Eds. *Molten salt chemistry*. NATO ASI Series C, Holland, D. Reidel Co, vol. 202 (1987) p. 217.
- [7] A.L. Rollet, M. Salanne, Studies of the local structures of molten metal halides, *Annu. Rep. Prog. Chem. Sect. C. Phys. Chem.*, 107 (2011) 88-123.
- [8] A. Strecker, Ueber die künstliche Bildung der Milchsäure und einen neuen, dem Glycocoll homologen Körper, *Liebigs. Ann. Chem.*, 75 (1850) 27-45.
- [9] (a) R. Sridhar, P.T. Perumal, A new protocol to synthesize 1,4-dihydropyridines by using 3,4,5-trifluorobenzenboronic acid as a catalyst in ionic liquid: synthesis of novel 4-(3-carboxyl-1H-pyrazol-4-yl)-1,4-dihydropyridines, *Tetrahedron*, 61 (2005) 2465-2470; (b) S. Tu, B. Jiang, R. Jia, J. Zhang, Y. Zhang., An efficient and expeditious microwave-assisted synthesis of 4-azafluorenones via a multi-component reaction, *Tetrahedron Lett.*, 48 (2007) 1369-1374; (c) M. Sayyafi, M. Seyyedhamzeh, H.R. Khavasi, A. Bazgir, One-pot, three-component route to 2H-indazolo[2,1-b]phthalazine-triones, *Tetrahedron*, 64 (2008) 2375-2378; (d) Ch. Liu, L. Zhou, D. Jiang, Y. Gu, Multicomponent reactions of Aldo-X bifunctional reagent α -oxoketene dithioacetals and indoles or amines: divergent synthesis of dihydrocoumarins, quinolines, furans, and pyrroles, *Asian J. Org. Chem.*, 5 (2016) 367-372.
- [10] M. Darbarwar, V. Sundarmurthy, Synthesis of coumarins with 3:4-fused ring systems and their physiological activity, *Synthesis*, 5 (1982) 337-388.

- [11] (a) L. Loy, G. Bonsignore, D. Secci, A. Calignano, Synthesis and pharmacological activity of 2-oxo-(2H)1-benzopyran-3-carboxamide derivatives, *Eur. J. Med. Chem.*, 28 (1993) 517-520; (b) S.J. Tu, H. Jiang, Q.Y. Zhuang, C.B. Miao, D.Q. Shi, X.S. Wang, Y. Gao, One-pot synthesis of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzo[b]pyran under ultrasonic irradiation without catalyst, *Chin. J. Org. Chem.*, 23 (2003) 488-490.
- [12] C.S. Konkoy, D.B. Fick, S.X. Cai, N.C. Lan, J.F.W. Kenna, Substituted 5-oxo-5,6,7,8-tetrahydro-4H-1-benzopyrans and benzothiopyrans and the use thereof as potentiators of AMPA, WO 0075123 (2000); *Chem. Abstr.* 134 (2001) 29313a.
- [13] X.S. Wang, D.Q. Shi, S.J. Tu, C.S. Yao, A convenient synthesis of 5-oxo-5, 6, 7, 8-tetrahydro-4 H-benzo-[b]-pyran derivatives catalyzed by KF-alumina, *Synth. Commun.*, 33 (2003) 119-126.
- [14] T.S. Jin, A.Q. Wang, X. Wang, J.S. Zhang, T.S. Li, A clean one-pot synthesis of tetrahydrobenzo[b]pyran derivatives catalyzed by hexadecyltrimethyl ammonium bromide in aqueous media, *Synlett*, (2004) 871-873.
- [15] L. Fotouhi, M.M. Heravi, A. Fatehi, K. Bakhtiari, Electrogenated base-promoted synthesis of tetrahydrobenzo[b]pyran derivatives, *Tetrahedron Lett.*, 48 (2007) 5379-5381.
- [16] S. Balalaie, M. Sheikh-Ahmadi, M. Bararjanian, Tetra-methyl ammonium hydroxide: An efficient and versatile catalyst for the one-pot synthesis of tetrahydrobenzo[b]pyran derivatives in aqueous media, *Catal. Commun.*, 8 (2007) 1724-1728.
- [17] Y.Q. Peng, G.H. Song, Amino-functionalized ionic liquid as catalytically active solvent for microwave-assisted synthesis of 4H-pyrans, *Catal. Commun.*, 8 (2007) 111-114.

- [18] J.Y.C. Wu, W.F. Fong, J.X. Zhang, C.H. Leung, H.L. Kwong, M.S. Yang, D. Li, H.Y. Cheung, Reversal of multidrug resistance in cancer cells by pyranocoumarins isolated from *Radix Peucedani*, *Eur. J. Pharmacol.*, 473 (2003) 9-17.
- [19] N.R. Emmadi, K. Atmakur, G.K. Chityal, S. Pombala, J.B. Nanubolu, Synthesis and cytotoxicity evaluation of highly functionalized pyranochromenes and pyranopyrans, *Bioorg. Med. Chem. Lett.*, 22 (2012) 7261-7264.
- [20] G. Cingolani, F. Gualtieri, M. Pigini, Researches in the field of antiviral compounds. Mannich bases of 3-hydroxycoumarin, *J. Med. Chem.*, 12 (1969) 531-532.
- [21] L. Bonsignore, G. Loy, D. Secci, A. Calignano, Synthesis and pharmacological activity of 2-oxo-(2H) 1-benzopyran-3-carboxamide derivatives, *Eur. J. Med. Chem.*, 28 (1993) 517-520.
- [22] F.W. Perrella, S.F. Chen, D.L. Behrens, R.F. Kaltenbach, S.P. Seitz, Phospholipase C inhibitors: a new class of agents, *J. Med. Chem.*, 37 (1994) 2232-2237.
- [23] (a) Y. Kashman, K.R. Gustafson, R.W. Fuller, J.H. Cardellina, J.B. McMahon, M.J. Currens, R.W. Buckheit, S.H. Hughes, G.M. Cragg, M.R. Boyd, HIV inhibitory natural products. Part 7. The calanolides, a novel HIV-inhibitory class of coumarin derivatives from the tropical rainforest tree, *Calophyllum lanigerum*, *J. Med. Chem.*, 35 (1992) 2735-2743; (b) A.D. Patil, A.J. Freyer, D.S. Eggleston, R.C. Haltiwanger, M.F. Bean, P.B. Taylor, M.J. Caranfa, A.L. Breen, H.R. Bartus, The inophyllums, novel inhibitors of HIV-1 reverse transcriptase isolated from the Malaysian tree, *Calophyllum inophyllum* Linn, *J. Med. Chem.*, 36 (1993) 4131-4138.
- [24] J.M. Khurana, B. Nand, P. Saluja, DBU: a highly efficient catalyst for one-pot synthesis of substituted 3,4-dihydropyrano[3,2-c]chromenes, dihydropyrano[4,3-b]pyranes, 2-amino-4H-benzo[h]chromenes and 2-amino-4H benzo[g]chromenes in aqueous medium, *Tetrahedron*, 66 (2010) 5637-5641.

- [25] S. Paul, P. Bhattacharyya, A.R. Das, One-pot synthesis of dihydropyrano[2,3-c]chromenes via a three component coupling of aromatic aldehydes, malononitrile, and 3-hydroxycoumarin catalyzed by nano-structured ZnO in water: a green protocol, *Tetrahedron Lett.*, 52 (2011) 4636-4641.
- [26] J.M. Khurana, S. Kumar, Tetrabutylammonium bromide (TBAB): a neutral and efficient catalyst for the synthesis of biscoumarin and 3,4-dihydropyrano[c]chromene derivatives in water and solvent-free conditions, *Tetrahedron Lett.*, 50 (2009) 4125-4127.
- [27] R.M. Shaker, Synthesis and reactions of some new 4H-pyrano [3,2-c] benzopyran-5-one derivatives and their potential biological activities, *Pharmazie*, 51 (1996) 148-151.
- [28] M.M. Heravi, M. Zakeri, N. Mohammadi, Morpholine catalyzed one-pot multicomponent synthesis of compounds containing chromene core in water, *Chin. J. Chem.*, 29 (2011) 1163-1166.
- [29] (a) M.A. Zolfigol, S. Baghery, A.R. Moosavi-Zare, S.M. Vahdat, H. Alinezhad, M. Norouzi, Design of 1-methylimidazolium tricyanomethanide as the first nanostructured molten salt and its catalytic application in the condensation reaction of various aromatic aldehydes, amides and β -naphthol compared with tin dioxide nanoparticles, *RSC. Adv.*, 5 (2015) 45027-45037; (b) M.A. Zolfigol, S. Baghery, A.R. Moosavi-Zare, S.M. Vahdat, H. Alinezhad, M. Norouzi, Synthesis of the first nano ionic liquid 1-methylimidazolium trinitromethanide {[HMIM]C(NO₂)₃} and its catalytic use for Hantzsch four-component condensation, *RSC. Adv.*, 4 (2014) 57662-57670; (c) M.A. Zolfigol, S. Baghery, A.R. Moosavi-Zare, S.M. Vahdat, Synthesis of 1,2,4,5-tetrasubstituted imidazoles using 2,6-dimethylpyridinium trinitromethanide {[2,6-DMPyH]C(NO₂)₃} as a novel nanostructured molten salt and green catalyst, *RSC. Adv.*, 5 (2015) 32933-32940; (d) M.A. Zolfigol, F. Afsharnadery, S. Baghery, S.

- Salehzadeh, F. Maleki, Catalytic applications of {[HMIM]C(NO₂)₃}: as a nano ionic liquid for the synthesis of pyrazole derivatives under green conditions and a mechanistic investigation with a new approach, *RSC Adv.*, 5 (2015) 75555-75568; (e) M.A. Zolfigol, S. Baghery, A.R. Moosavi-Zare, S.M. Vahdat, Synthesis and characterization of new 1-(α -aminoalkyl)-2-naphthols using pyrazine-1,4-dium trinitromethanide {[1,4-DHPyrazine][C(NO₂)₃]₂} as a novel nano-structured molten salt and catalyst in compared with Ag–TiO₂ nano composite, *J. Mol. Catal. A. Chem.*, 409 (2015) 216-226.
- [30] V.K. Das, R.R. Devi, P.K. Raul, A.J. Thakur, Nano rod-shaped and reusable basic Al₂O₃ catalyst for N-formylation of amines under solvent-free conditions: A novel, practical and convenient ‘NOSE’ approach, *Green Chem.*, 14 (2012) 847-854.
- [31] (a) P. Salehi, M.A. Zolfigol, F. Shirini and M. Baghbanzadeh, Silica sulfuric acid and silica chloride as efficient reagents for organic reactions, *Curr. Org. Chem.*, 10 (2006) 2171-2189; (b) A. Khazaei, M.A. Zolfigol, M. Mokhlesi, R. Rostamian, Nano-sphere silica sulfuric acid: novel and efficient catalyst in the one-pot multi-component synthesis, *J. Iran. Chem. Soc.*, 10 (2013) 1297-1301; (c) M. Daraei, M.A. Zolfigol, F. Derakhshan-Panah, M. Shiri, H.G. Kruger, M. Mokhlesi, Synthesis of tetrahydropyridines by one-pot multicomponent reaction using nano-sphere silica sulfuric acid, *J. Iran. Chem. Soc.*, 12 (2015) 855-861; (d) D. Azarifar, S.M. Khatami, M.A. Zolfigol, R. Nejat-Yami, Nano-titania sulfuric acid-promoted synthesis of tetrahydrobenzo [b] pyran and 1, 4-dihydropyrano [2, 3-c] pyrazole derivatives under ultrasound irradiation, *J. Iran. Chem. Soc.*, 11 (2014) 1223-1230; (e) M. Safaiee, M.A. Zolfigol, M. Tavasoli, M. Mokhlesi, Application of silica vanadic acid [SiO₂-VO(OH)₂] as a heterogeneous and recyclable catalyst for oxidative aromatization of Hantzsch 1,4-dihydropyridines at room temperat, *J. Iran. Chem. Soc.*, 11 (2014) 1593-1597.

- [32] F. Shirini, M.A. Zolfigol, P. Salehi, M. Abedini, Applications of some metal hydrogen sulfates in organic transformations, *Curr. Org. Chem.*, 12 (2008) 183-202.
- [33] M.A. Zolfigol, R. Ayazi-Nasrabadi, S. Baghery, Synthesis and characterization of two novel biological-based nano organo solid acids with urea moiety and their catalytic applications in the synthesis of 4,4'-(arylmethylene)bis(1H-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives under mild and green conditions, *RSC Adv.*, 5 (2015) 71942-71954.
- [34] (a) E. Mosaddegh, A. Hassankhani, G. Mansouri, An efficient, simple and green Zn (Phen) 2Cl_2 complex catalyzed synthesis of 4-H-benzo [b] pyrans in water at ambient temperature, *E-J. Chem.*, 8 (2011) 529-534; (b) B.C. Ranu, S. Banerjee, S. Roy, A task specific basic ionic liquid,[bmIm] OH-promoted efficient, green and one-pot synthesis of tetrahydrobenzo [b] pyran derivatives, *Indian J. Chem.*, 47B (2008) 1108-1112; (c) A. Hasaninejad, N. Jafarpour, M. Mohammadnejad, Synthesis of benzo[b]pyrane derivatives using supported potassium fluoride as an efficient and reusable catalytic system, *E-J. Chem.*, 9 (2012) 2000-2005; (d) K.S. Niralwad, K.F. Shelke, S.S Sadaphal, B.B. Shingate, M.S. Shingare, An efficient and green synthesis of tetrahydrobenzo [b] pyran derivatives catalysed by sodium hypochlorite by grinding, *Bull. Catal. Soc. India.*, 8 (2009) 188-192; (e) K. Tabatabaeian, H. Heidari, M. Mamaghani, N. Mahmoodi, Ru(II) complexes bearing tertiary phosphine ligands: a novel and efficient homogeneous catalyst for one-pot synthesis of dihydropyrano[3,2-c]chromene and tetrahydrobenzo[b]pyran derivatives, *Appl. Organometal. Chem.*, 26 (2012) 56-61; (f) K.A. Undale, Y.K. Park, K. Park, D.H. Dagade, D.M. Pore, A revisit to the Hantzsch reaction: unexpected formation of tetrahydrobenzo[b]pyrans beyond polyhydroquinolines, *Synlett*, 6 (2011) 791-796.

- [35] (a) H. Mehrabi, H. Abusaidi, Synthesis of biscoumarin and 3, 4-dihydropyrano[c]chromene derivatives catalysed by sodium dodecyl sulfate (SDS) in neat water, *J. Iran. Chem. Soc.*, 7 (2010) 890-894; (b) S. Balalaie, S. Abdolmohammadi, Novel and efficient catalysts for the one-pot synthesis of 3,4-dihydropyrano[c]chromene derivatives in aqueous media, *Tetrahedron Lett.*, 48 (2007) 3299-3303; (c) K. Niknam, A. Jamali, Silica-Bonded N-Propylpiperazine Sodium n-Propionate as Recyclable Basic Catalyst for Synthesis of 3,4-Dihydropyrano[c]chromene Derivatives and Biscoumarins, *Chin. J. Catal.*, 33 (2012) 1840-1849; (d) M. Safaiee, M.A. Zolfigol, F. Afsharnadery, S. Bagheri, Synthesis of a novel dendrimer core of oxo-vanadium phthalocyanine magnetic nano particles: as an efficient catalyst for the synthesis of 3,4-dihydropyrano[c]chromenes derivatives under green condition, *RSC. Adv.*, 2015, 5, 102340-102349; (e) J.P. Patel, J.R. Avalani, D.K. Raval, Polymer supported sulphanilic acid: A highly efficient and recyclable green heterogeneous catalyst for the construction of 4,5-dihydropyrano[3,2-c]chromenes under solvent-free conditions, *J. Chem. Sci.*, 125 (2013) 531-537; (f) A. Shaabani, S. Samadi, Z. Badri, A. Rahmati, Ionic liquid promoted efficient and rapid one-pot synthesis of pyran annulated heterocyclic systems, *Catal. Lett.*, 104 (2005) 39-43; (g) M. Khoobi, L. Ma'mani, F. Rezazadehb, Z. Zareieb, A. Foroumadi, A. Ramazani, A. Shafiee, One-pot synthesis of 4H-benzo[b]pyrans and dihydropyrano[c]chromenes using inorganic–organic hybrid magnetic nanocatalyst in water, *J. Mol. Catal. A: Chem.*, 359 (2012) 74-80.

Scheme, Table and Figure section:

Scheme 1. The synthesis of tetrahydrobenzo[*b*]pyran and 3,4-dihydropyrano[*c*]chromene derivatives in the presence of $\{[HMIM][C(CN)_3]\}$ as a NMS catalyst.

Table 1. Result of amount of the catalyst and temperature on the condensation reaction of 2,5-dimethoxybenzaldehyde, malononitrile and dimedone under solvent-free conditions.^a

Entry	Catalyst amount (mol%)	Reaction temperature (°C)	Reaction time (min)	Yield ^b (%)
1	—	r.t.	60	40
2	—	100	60	50
3	0.5	r.t.	8	95
4	0.5	75	8	95
5	0.5	100	8	95
6	1	r.t.	8	95
7	1	100	8	95
8	2	r.t.	8	95
9	2	100	8	95
10	5	r.t.	10	94
11	10	r.t.	10	94

Reaction conditions: ^a 2,5-Dimethoxybenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol); ^b Isolated yield.

Table 2. The effect of different solvents on the reaction of 2,5-dimethoxybenzaldehyde, malononitrile and dimedone catalyzed by nano molten salt (0.5 mol%) at room temperature.^a

Entry	Solvent	Reaction time (min)	Yield ^b (%)
1	Solvent-free	8	95
2	H ₂ O	10	94
3	C ₂ H ₅ OH	10	94
4	CH ₃ CN	15	93
5	CH ₃ CO ₂ Et	20	88
6	CH ₂ Cl ₂	20	91

Reaction conditions: ^a 2,5-Dimethoxybenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol); ^b Isolated yield.

Table 3. Synthesis of tetrahydrobenzo[*b*]pyran derivatives using {[HMIM]C(CN)₃} as a nano structure molten salt catalyst.^a

Entry	Aldehyde	Time (min)	Yield ^b (%)	M.p (°C) [Ref.]
1		5	97	206-208 [34a] (White)
2		8	96	200-202 [34b] (Cream)
3		8	96	216-218 [34c] (White)
4		10	95	210-212 [34d] (Brown)
5		3	98	229-231 [34e] (White)

6		10	95	218-220 (White)
7		15	93	226-228 [34c] (White)
8		5	97	214-216 [34a] (Violet)
9		20	92	247-249 ^{dec} (Yellow)
10		15	92	181-183 (Orange)
11		8	95	181-183 (Cream)
12		8	95	164-166 [34f] (Cream)
13		10	94	273-275 (White)
14		15	92	182-184 (Brown)
15		8	96	218-220 [34a] (Brown)
16		15	92	223-225 [34b] (White)
17		15	92	222-224 [34b] (White)

18		20	92	249-251 (Orange)
19		20	92	241-243 (White)
20		3	98	157-159 [34b] (White)

Reaction conditions: ^a 2,5-Dimethoxybenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), {[HMIM]C(CN)₃} as a NMS catalyst (0.5 mol%), Solvent-free, r.t.; ^b Isolated yield.

Scheme 2. The suggested mechanism for the synthesis of tetrahydrobenzo[*b*]pyran derivatives *via* tandem Knoevenagel-Michael cyclocondensation using {[HMIM]C(CN)₃} as a NMS catalyst.

Fig. 1. Reusability of {[HMIM]C(CN)₃} as a NMS catalyst on the synthesis of tetrahydrobenzo[*b*]pyran in 8 minutes.

Table 4. Result of amount of the catalyst and temperature on the condensation reaction of 2,5-dimethoxybenzaldehyde, malononitrile and 4-hydroxycoumarin under solvent-free conditions.^a

Entry	Catalyst amount (mol%)	Reaction temperature (°C)	Reaction time (min)	Yield ^b (%)
1	—	r.t.	60	30
2	—	100	60	45
3	0.5	r.t.	10	94
4	0.5	75	10	94
5	0.5	100	10	94
6	1	r.t.	10	94
7	1	100	10	94
8	2	r.t.	10	93
9	2	100	10	93
10	5	r.t.	15	92
11	10	r.t.	15	92

Reaction conditions: ^a 2,5-Dimethoxybenzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol); ^b Isolated yield.

Table 5. The effect of different solvents on the reaction of 2,5-dimethoxybenzaldehyde, malononitrile and 4-hydroxycoumarin catalyzed by nano molten salt (0.5 mol%) at room temperature.^a

Entry	Solvent	Reaction time (min)	Yield ^b (%)
1	Solvent-free	10	94
2	H ₂ O	15	93
3	C ₂ H ₅ OH	15	93
4	CH ₃ CN	20	90
5	CH ₃ CO ₂ Et	30	85
6	CH ₂ Cl ₂	30	88

Reaction conditions: ^a 2,5-Dimethoxybenzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol); ^b Isolated yield.

Table 6. Synthesis of 3,4-dihydropyrano[*c*]chromene derivatives using [HMIM]C(CN)₃ as a nano structure molten salt catalyst.^a

Entry	Aldehyde	Time (min)	Yield ^b (%)	M.p (^o C) ^{Ref.}
1		5	97	268-271 [35a] (White)
2		3	98	260-262 [35a] (Yellow)
3		10	96	235-237 [35b] (White)
4		10	96	255-257 [35a] (White)
5		15	94	260-262 [35c] (White)

6		5	97	261-263 [35d] (White)
7		12	95	248-250 [35d] (White)
8		20	92	248-250 [35c] (White)
9		5	97	262-264 [35a] (White)
10		25	91	235-237 [35e] (Yellow)
11		18	92	231-233 (Orange)
12		10	94	258-260 [35f] (White)
13		8	94	217-219 [35a] (White)
14		15	93	296-298 [35d] (White)
15		20	90	272-274 [35g] (Brown)
16		10	95	258-260 [35a] (White)

17		20	90	245-247 [35g] (White)
18		20	90	223-225 [35e] (Cream)
19		25	90	228-230 (Orange)
20		20	90	208-210 (Brown)

Reaction conditions: ^a 2,5-Dimethoxybenzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), {[HMIM]C(CN)₃} as a NMS catalyst (0.5 mol%), Solvent-free, r.t.; ^b Isolated yield.

Scheme 3. The probable mechanism for the synthesis of 3,4-dihydropyrano[c]chromenederivatives using {[HMIM]C(CN)₃} as a NMS catalyst.

Fig. 2. Reusability of $\{[\text{HMIM}]\text{C}(\text{CN})_3\}$ as a NMS catalyst on the synthesis of 3,4-dihydropyrano[*c*]chromene in 10 minutes.