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Application of {[4,4′-BPyH][C(CN)$_3$]$_2$} as a Bifunctional Nanostructured Molten Salt Catalyst for the Preparation of 2-Amino-4*H*-chromene Derivatives under Solvent-Free and Benign Conditions

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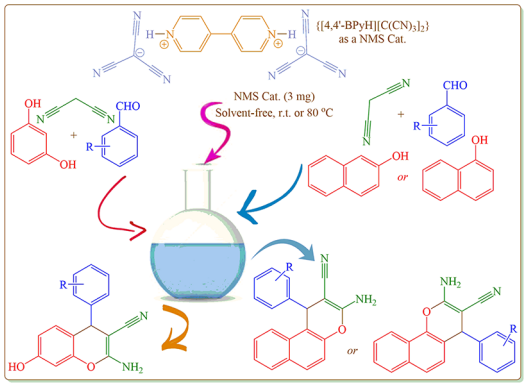

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Abstract The bifunctional nanostructured molten salt [4,4′-bipyridine]-1,1′-diium tricyanomethanide has been employed as a highly efficient and powerful catalyst for the preparation of 2-amino-4*H*-chromenes. A wide variety of aromatic aldehydes was condensed with malononitrile and resorcinol, 1-naphthol or 2-naphthol under mild and solvent-free conditions. This protocol has the advantages of short reaction times, high to excellent yields, and straightforward workup.

Key words multicomponent reactions, molten salt, ionic liquids, solvent-free conditions

The success of multicomponent reactions (MCRs) has persuaded both academic and industrial communities to use this approach to access molecular diversity. The advantages of this methodology include fabrication of various new chemical bonds in one-pot with high atomic economy, a reduction in both the number of by-products formed and the number of purification steps required, and the ease of workup.[1]

2-Amino-4*H*-chromenes have been applied to the treatment of rheumatoid arthritis, psoriasis, cancer, amyotrophic lateral sclerosis, Parkinson's disease, Huntington's disease, Alzheimer's disease, Down's syndrome, AIDS, schizophrenia, and myoclonus,[2] as well as demonstrating biological properties such as antiviral,[3] antimicrobial,[4] antiproliferative,[5] mutagenic,[6] antitumor,[7] pheromonal,[8] and central nervous system activity.[9] Furthermore, 2-amino-4*H*-chromene derivatives have been exploited as laser dyes,[10] optical brighteners,[11] fluorescence markers,[12] pigments,[13] cosmetics, and biodegradable agrochemicals.[14]

Several homogeneous and heterogeneous catalysts have been employed for the synthesis of 2-amino-4*H*-chromene derivatives, including aminosilane-modified Fe_3O_4 nanoparticles,[15] potassium phthalimide-*N*-oxyl,[16] gel entrapped DABCO,[17] Fe_3O_4-chitosan MNPs,[18] Mg/Al-HT,[19] TAFMC-1,[20] nanozeolite clinoptilolite,[21] anhydrous sodium carbonate,[22] TPOP-2,[23] a nano-polypropylenimine dendrimer,[24] potassium phthalimide,[25] $TiCl_4$,[26] methane sulfonic acid,[27] $InCl_3$,[28] γ-alumina,[29] and tetramethylguanidine.[30] Although, these reported protocols have their merits, they also suffer from one or more drawbacks. Hence, the development of milder methods that can be conducted under solvent-free conditions employing environmentally benign catalysts is still a valid goal.

Ionic liquids (ILs) and molten salts (MSs) play key roles in extraction, as reactive catalytic supports and spatial devices, and in biotransformations.[31] In general, ILs and MSs differ with respect to the region of their melting point. Whereas ionic liquids melt at or near ambient temperature, molten salts or fused salts tend to have higher melting points, generally considered to be over 100 °C.[32] Recently, Atkin et al. considered structure and nanostructure in ionic liquids[33] and a reductive Friedel–Crafts alkylation was studied without using external reductant.[34] Following our previous studies on the design, synthesis, and applications of nano-ionic liquids and molten salts in organic reactions[35] and as a part of our continuing investigations on strategies for one-pot multicomponent reactions for the preparation of pharmaceutical and biological consequential molecules,[36] herein, we report the preparation of a wide range of 2-amino-4*H*-chromenes through the reaction of various aryl aldehydes, malononitrile, resorcinol, 1-naphthol or 2-naphthol under mild conditions in the presence of the first bifunctional nanostructured molten salt, {[4,4′-BPyH][C(CN)$_3$]$_2$}.

Table 1 Effect of Catalyst Loading and Influence of Solvent for the Model Reaction at Room Temperature[a]

Entry	Catalyst amount (mg)	Solvent	Reaction time (min)	Yield (%)[b]
1	1	–	50	30
2	2	–	20	86
3	3	–	10	94
4	4	–	9	94
5	5	–	9	95
6	3	EtOH	60	trace
7	3	H_2O	60	trace
8	3	CH_3CN	60	trace
9	3	$CHCl_3$	80	71
10	3	*n*-hexane	65	67
11	3	CH_2Cl_2	55	trace

[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), resorcinol (1 mmol).
[b] Isolated yield.

Initially, [4,4′-bipyridin]-1,1′-diium tricyanomethanide was produced as a bifunctional molten salt catalyst (see the Supporting Information). The catalytic applicability of the resulting nano-bifunctional molten salt was investigated for the preparation of 2-amino-4*H*-chromene derivatives. To optimize the reaction conditions, the condensation of 4-chlorobenzaldehyde, malononitrile, and resorcinol (1 mmol each) was selected as a typical reaction. The reaction was performed with different amounts of nano-bifunctional molten salt heated to 25–100 °C under solvent-free conditions (Table 1). The best results were obtained by using 3 mg nanostructured molten salt under solvent-free conditions at room temperature (entry 3). No improvement in yield was observed on increasing either the amount of catalyst or temperature. The reaction did not proceed in the absence of nanocatalyst.

To demonstrate the generality of this methodology for the synthesis of 2-amino-4*H*-chromenes, a range of aromatic aldehydes was condensed with malononitrile and resorcinol, 1-naphthol or 2-naphthol under solvent-free conditions (Table 2). For aromatic aldehydes bearing electron-

Table 2 Cascade Knoevenagel–Michael Cyclocondensation Sequence for the Synthesis of 2-Amino-4*H*-chromene Derivatives Using {[4,4′-BPyH][$C(CN)_3]_2$} as a Bifunctional Nanostructured Molten Salt Catalyst[a]

Entry	Arylaldehyde	Phenol	Time (min)	Temp. (°C)	Yield (%)[b]	Mp (°C) [Lit.][Ref.]
1	4-Cl	resorcinol	10	r.t.	94	239–241 [228–230]22
2	2,4-Cl_2	resorcinol	12	r.t.	94	256–258 [256–259]15
3	4-NO_2	resorcinol	12	r.t.	91	218–220 [210–212]19
4	4-Br	resorcinol	13	r.t.	92	251–253 [240–241]22
5	3-NO_2	resorcinol	14	r.t.	89	121–123 [188–190]19
6	benzaldehyde	resorcinol	15	80	90	238–240 [230–231]22
7	4-OMe	resorcinol	11	80	94	227–229 [109–111]15
8	4-(*N*,*N*-Me_2)	resorcinol	10	80	85	173–175 [190–192]16
9	3-OH	resorcinol	15	80	91	219–221 [215–217]15
10	3,4-$(OMe)_2$	resorcinol	13	80	84	227–229 [215–217]19
11	3-OMe	resorcinol	16	80	89	180–182
12	4-Cl	2-naphthol	15	80	91	219–221 [207–209]22
13	2,4-Cl_2	2-naphthol	15	80	90	240–242 [254–255]37
14	4-Cl	1-naphthol	10	80	94	239–241 [233–235]22
15	4-CN	1-naphthol	9	80	93	264–266 [259–260]37
16	4-OMe	1-naphthol	20	80	90	188–190 [191]17
17	2-Cl	1-naphthol	10	80	93	247–249 [240–241]25
18	4-Br	1-naphthol	8	80	92	249–251 [240–241]37
19	benzaldehyde	1-naphthol	20	80	85	215–216 [218–219]37
20	benzaldehyde	resorcinol	120	80	–	–38
21	benzaldehyde	2-naphthol	120	80	–	–38
22	benzaldehyde	1-naphthol	120	80	–	–38

[a] Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1 mmol), phenol derivatives (1 mmol), {[4,4′-BPyH][$C(CN)_3]_2$} as a nanostructure molten salt catalyst (3 mg), solvent-free.
[b] Isolated yield.

Table 3 Synthesis of 2-Amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile with Nanostructured Molten Salt Catalyst and with Previously Reported Catalysts

Entry	Reaction conditions	Catalyst loading	Time (min)	Yield (%)	Ref.
1	{[4,4′-BPyH][C(CN)$_3$]$_2$}, solvent-free, 80 °C	3 mg	15	90	this work
2	POPINO, H_2O, reflux	1.5 mol%	20	90	16
3	Na_2CO_3, grinding, 50 °C		30	92	39
4	Mg/Al-HT, H_2O, 60 °C	15 wt%	240	95	19
5	TAFMC-1, H_2O, 100 °C	30 mg	720	86	20
6	Nanozeolite CP, H_2O, reflux	0.01 g	15	92	21
7	TPOP-2, solvent-free, 80 °C	40 mg	300	87	23
8	DAB-PPI G1, solvent-free, 110 °C	15 mol%	20	82	24

withdrawing groups (entries 1–5), the reaction reached completion relatively rapidly, but for benzaldehyde and aromatic aldehydes, with electron-releasing groups, it was found that the reaction did not proceed at room temperature. Accordingly, as a model, we tested the reaction of benzaldehyde, malononitrile, and resorcinol at different temperatures; the best result was achieved at 80 °C, giving a product yield of 90% in 15 minutes. Hence, for benzaldehyde and aromatic aldehydes, bearing electron-releasing groups, the reaction was performed at 80 °C (entries 6–19).

In a further study, to optimize the reaction conditions for the synthesis of analogues, the condensation reaction of benzaldehyde, ethyl cyanoacetate, and resorcinol, β-naphthol or α-naphthol was chosen as a model system under solvent-free conditions at 80 °C (Table 2, entries 20–22). However, in these cases, no product was obtained after 2 hours.

The efficacy of this bifunctional nanostructured molten salt catalyst was compared with those of other catalysts for the synthesis of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile. To this end, we assessed the ability of these catalysts to promote the condensation of benzaldehyde with malononitrile and resorcinol (Table 3). It was found that the nanostructure molten salt catalyst compares favorably in this reaction.

In summary, the bifunctional nanostructure molten salt [4,4′-bipyridine]-1,1′-diium tricyanomethanide has been employed as a highly efficient and powerful catalyst for the preparation of 2-amino-4*H*-chromenes.[40]

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561345.

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(40) **General Procedure for the Preparation of Nanostructured Molten Salt {[4,4′-BPyH][C(CN)$_3$]$_2$}**
To an aqueous solution of tricyanomethane (0.455 g, 5 mmol, 5 mL), 4,4′-bipyridine (0.39 g, 2.5 mmol) was added and the resulting mixture was stirred for 3 h at ambient temperature. The solvent was then evaporated under reduced pressure. The pale-yellow powder was dried under vacuum at 100 °C for 3 h. The obtained pale-yellow solid was filtered, washed repeatedly with diethyl ether to remove any unreacted starting materials, and then dried under vacuum.

General Procedure for the Synthesis of 2-Amino-4*H*-chromene Derivatives through a Cascade Knoevenagel–Michael Cyclocondensation Sequence

To a mixture of aryl aldehyde (1 mmol), malononitrile (0.066 g, 1 mmol), and phenol (1 mmol) in a round-bottom flask, [4,4′-bipyridine]-1,1′-diium tricyanomethanide (3 mg) was added and the mixture was stirred at either room temperature (Table 2, entries 1–5) or 80 °C (entries 6–19) in the absence of solvent for the appropriate time (Table 2). After completion of the reaction as monitored by TLC (*n*-hexane/ethyl acetate, 2:1), ethyl acetate (10 mL) was added and the reaction mixture was stirred and heated to reflux for 10 min. The resulting mixture was then washed with water (10 mL) and decanted to separate catalyst from the other materials (the reaction mixture was soluble in hot ethyl acetate and nanostructured molten salt catalyst was soluble in water). The aqueous layer was decanted, separated, and the water was removed to recover the catalyst for further use. The organic layer was dried, filtered, the solvent was removed, and the crude product was purified by recrystallization from ethanol (95%) to give the pure product with high to excellent yields (Table 2).

Selected Characterization Data

2-Amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (Table 2, Entry 1)

Yield: 94% (0.280 g); mp 239–241 °C. FTIR (KBr): 3463, 3343, 3251, 2193, 1643, 1506, 1402, 1154, 1111 cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 4.67 (s, 1 H, CH), 6.42 (d, ^4J = 2 Hz, 1 H, ArH), 6.50 (dd, ^3J= 8 Hz, ^4J = 2 Hz, 1 H, ArH), 6.79 (d, ^3J = 8 Hz, 1 H, ArH), 6.92 (s, 2 H, NH$_2$), 7.19 (d, ^3J = 8 Hz, 2 H, ArH), 7.37 (d, ^3J = 8 Hz, 2 H, ArH), 9.73 (s, 1 H, OH). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 55.8, 102.2, 112.4, 113.2, 120.5, 128.5, 129.3, 129.9, 131.2, 145.3, 148.8, 157.2, 160.2.

2-Amino-4-(4-bromophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (Table 2, Entry 4)

Yield: 92% (0.315 g); mp 251–253 °C. FTIR (KBr): 3470, 3340, 3256, 2191, 1640, 1507, 1411, 1155, 1112 cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 4.66 (s, 1 H, CH), 6.42 (d, ^4J = 2.4 Hz, 1 H, ArH), 6.50 (dd, ^3J = 8 Hz, ^4J = 2.4 Hz, 1 H, ArH), 6.80 (m, 1 H, ArH), 6.92 (s, 2 H, NH$_2$), 7.13 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.50 (d, ^3J = 8.4 Hz, 2 H, ArH), 9.74 (s, 1 H, OH). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 55.7, 102.2, 112.5, 113.1, 119.7, 120.5, 129.6, 129.9, 131.5, 145.7, 148.8, 157.2, 160.2.

2-Amino-7-hydroxy-4-(3-methoxyphenyl)-4*H*-chromene-3-carbonitrile (Table 2, Entry 11)

Yield: 89% (0.262 g); mp 180–182 °C. FTIR (KBr): 3446, 3340, 3219, 2192, 1641, 1508, 1410, 1154, 1115, 1048 cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 3.72 (s, 3 H, OMe), 4.59 (s, 1 H, CH), 6.41 (d, ^4J = 2.4 Hz, 1 H, ArH), 6.49 (dd, ^3J = 8 Hz, ^4J = 2.4 Hz, 1 H, ArH), 6.72–6.85 (m, 4 H, ArH), 6.87 (s, 2 H, NH$_2$), 7.23 (t, ^3J = 8 Hz, 1 H, ArH), 9.67 (s, 1 H, OH). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 54.9, 56.1, 102.1, 111.5, 112.3, 113.4, 113.6, 119.5, 120.6, 129.7, 129.8, 147.9, 148.8, 157.1, 159.3, 160.3.

3-Amino-1-(4-dichlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (Table 2, Entry 13)

Yield: 90% (0.331 g); mp 240–242 °C. FTIR (KBr): 3463, 3324, 3190, 2200, 1661, 1589, 1407, 1237, 819 cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 5.72 (s, 1 H, CH), 7.03 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.11 (s, 2 H, NH$_2$), 7.27 (dd, ^3J = 8.4 Hz, ^4J = 2 Hz, 1 H, ArH), 7.35 (d, ^3J = 8.8 Hz, 1 H, ArH), 7.43–7.52 (m, 2 H, ArH), 7.58 (d, ^3J = 8.4 Hz, 1 H, ArH), 7.64 (d, ^4J = 2.4 Hz, 1 H, ArH), 7.94–7.99 (m, 2 H, ArH). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 55.0, 114.0,

118.2, 120.5, 120.6, 122.7, 123.8, 126.3, 126.6, 126.7, 127.6, 128.7, 132.6, 137.8, 142.6, 158.1, 159.9.

2-Amino-4-(4-methoxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 2, Entry 16)

Yield: 90% (0.296 g); mp 188–190 °C. FTIR (KBr): 3415, 3324, 2194, 1663, 1604, 1509, 1377, 1253, 1104, 1023, 809 cm^{-1}. ^1H NMR (400.13 MHz, DMSO-d_6): δ = 3.72 (s, 3 H, OMe), 4.85 (s, 1 H, CH), 6.88 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.10 (m, 1 H, NH_2 and 1 H, ArH), 7.17 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.56–7.66 (m, 4 H, ArH), 7.89 (d, ^3J = 8 Hz, 1 H, ArH), 8.24 (d, ^3J = 8 Hz, 1 H, ArH).

^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 34.8, 55.7, 114.1, 116.8, 119.7, 122.5, 125.1, 127.5, 128.5, 128.7, 128.9, 129.9, 130.1, 130.8, 131.4, 131.9, 132.1, 141.7, 147.1, 159.8.