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RESEARCH PAPER

A new approach for the synthesis of 3,4-dihydropyrano[c] chromenes and biscoumarins using {[2,2'-BPyH][C(CN)$_3$]$_2$} as a bifunctional nanostructured ionic liquid catalyst

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ABSTRACT

[2,2'-Bipyridine]-1,1'-diium tricyanomethanide {[2,2'-BPyH][C(CN)$_3$]$_2$} as a bifunctional nanostructured ionic liquid catalyst (0.5 mol%) was used for the synthesis of 3,4-dihydropyrano[*c*]chromenes (14 examples) under solvent-free condition at room temperature in high yield (82-91%) and short reaction time. In addition, the described ionic liquid catalyst was also applied for the synthesis of biscoumarins (8 examples) under the same reaction condition in good yield (87-91%) and short reaction time. The {[2,2'-BPyH][C(CN)$_3$]$_2$} as a catalyst was attained by the reaction of 2,2'-Bipyridine (5 mmol) and 5 mL of an aqueous solution of tricyanomethane (5 mmol) at room temperature for 3 hours. The {[2,2'-BPyH][C(CN)$_3$]$_2$} as a catalyst was obtained with high purity approved by FTIR, ^{1}H NMR, ^{13}C NMR, mass, TG, DTA, XRD, SEM, TEM analyses and melting-point determination. The catalyst was recovered in excellent yield and was used in the revealed reaction 5 times without the need of additional catalyst. The major advantages of the presented procedure are efficient catalysis and good cost efficiency.

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INTRODUCTION

Chromenes are substantial components of pharmacologically active compounds, as these systems have shown a wide range of biological activities such as antimicrobial [1,2], central nervous system (CNS) activities [3], antiviral [4], antitumor [5], antiproliferative [6], mutagenicity [7] and inhibitors of inluenza virus sialidases [8, 9]. Numerous methods have been reported for the synthesis of 3,4-dihydropyrano[*c*]chromenes, such as using piperidine and pyridine [10], nanostructured ZnO [11], tetrabutylammonium bromide [12], DBU [13], diammonium hydrogen phosphate [14], K_2CO_3 under microwave irradiation [15], 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)$_3$} [16-18], AVOPc-MNPs [19, 20, 21] and morpholine [22].

Coumarins occupy a significant place in the realm of natural products and synthetic organic chemistry. They have been used as anticoagulants [23], in the synthesis of insecticides, optical brighteners [24], additives in food and cosmetics [25], dispersed fluorescent and laser dyes [26]. Biscoumarins, the bridge substituted dimers of 4-hydroxycoumarin, have vast potential as anticoagulants [27, 28]. Various procedures have been reported for the synthesis of biscoumarin e.g., sodium dodecyl sulfate (SDS) [29], heteropolyacids [30], [bmim]BF_4 [31] CuO–CeO_2 [32], molecular iodine [33], {Fe_3O_4@SiO_2@$(CH_2)_3$semicarbazide-SO_3H/HCl} [34], phosphotungstic acid [35] and

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sonochemical condition [36].

Ionic liquids (ILs) have received increasing attention because of their exclusive characteristics as solvents: non-flammability, broad use temperature ranges, ionic conductivity, low vapor pressure and thermal stability [37-40]. These liquids are principally derived from organic cationic cores and non-coordinating anions that together form salts with weak interionic interactions that lower melting points to near room temperature [41].

In continuation of our studies in designing the ionic liquid catalyst and multi component reactions [16-21], we report here a solvent-free synthesis of 3,4-dihydropyrano[*c*]chromenes and biscoumarins in high isolated yield using 0.5 mol% of [2,2'-bipyridine]-1,1'-diium tricyanomethanide {[2,2'-BPyH][C(CN)$_3$]$_2$}[42] as a bifunctional nanostructured ionic liquid catalyst at room temperature (Scheme 1). The IL could be recycled and effectively reused for five subsequent runs. The procedure holds well without the need of additional catalyst.

EXPERIMENT

General information

The materials were purchased from Merck, Fluka and Sigma-Aldrich and used without any additional purification. All reactions were monitored *via* thin layer chromatography (TLC) on gel F254 plates. Fourier transform-infrared spectra of the samples were recorded on a Perkin–Elmer FT-IR spectrometer 17259 using KBr disks. NMR spectroscopy (^{1}H NMR 250 MHz and ^{13}C NMR 62) was studied in pure deuterated DMSO with tetramethylsilane (TMS) as the internal standard.

General procedure for the synthesis of [2,2'-bipyridine]-1,1'-diium tricyanomethanide {[2,2'-BPyH][C(CN)$_3$]$_2$}.

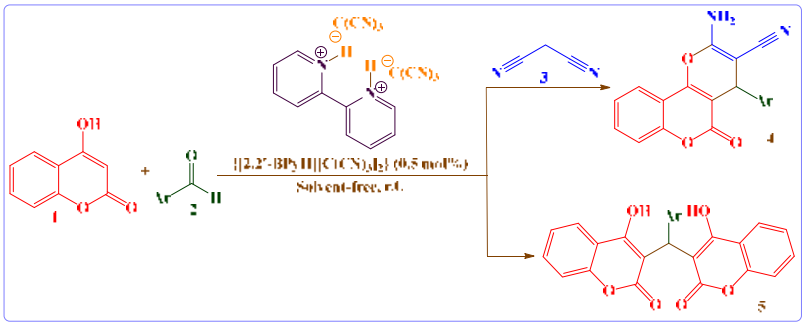
2,2'-Bipyridine (5 mmol: 0.781 g) was added to 5 mL of an aqueous solution of tricyanomethane (5 mmol: 0.455 g) and stirred at room temperature for 3 h. Subsequently, the solvent was evaporated by distillation under reduced pressure and the brown residue was dried under vacuum at 100 °C for 3 h. A brown solid produced which was filtered, washed with diethyl ether three times and dried under vacuum. The [2,2'-bipyridine]-1,1'-diium tricyanomethanide {[2,2'-BPyH][C(CN)$_3$]$_2$} catalyst was obtained with high purity approved by FTIR, ^{1}H NMR, ^{13}C NMR, mass, TG, DTA, XRD, SEM, TEM analyses and melting-point determination [42].

General procedure for the synthesis of 3,4-dihydropyrano[c]chromenes.

{[2,2'-BPyH][C(CN)$_3$]$_2$} as a NIL catalyst (0.5 mol%; 0.0017 g) was added to a mixture of various aldehyde (1 mmol), 4-hydroxycoumarin (1 mmol; 0.162 g) and malononitrile (1 mmol; 0.079 g) under solvent-free condition at room temperature for an appropriate time (Table 2). After completion of the reaction examined by TLC (*n*-hexane/ethyl acetate: 5/2), ethyl acetate (10 mL) was added to the reaction mixture, stirred and refluxed for 5 min, and 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 NIL catalyst was soluble in water). The solvent of organic layer was also removed and the crude product was recrystallized in ethanol.

General procedure for the synthesis of biscoumarins.

{[2,2'-BPyH][C(CN)$_3$]$_2$} as a NIL catalyst (0.5 mol%; 0.0017 g) was added to the mixture of various aldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol; 0.324 g) under solvent-free condition at room temperature for an appropriate time (Table 4). After completion of the reaction monitored by TLC (*n*-hexane/ethyl acetate: 5/2), ethyl acetate (10 mL) was added to the reaction mixture, stirred and



Scheme 1. Synthesis of 3,4-dihydropyrano[*c*]chromenes and biscoumarins using {[2,2'-BPyH][C(CN)$_3$]$_2$} as a NIL catalyst.

refluxed for 5 min, and 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 NIL catalyst was soluble in water). The solvent of organic layer was removed and the crude product was recrystallized in ethanol.

RESULTS AND DISCUSSION

Application of {[2,2'-BPyH][C(CN)$_3$]$_2$} as a NIL catalyst for the synthesis of 3,4-dihydropyrano[c] chromenes.

Firstly, we screened several solvents for the synthesis of 3,4-dihydropyrano[*c*]chromene from 4-nitrobenzaldehyde, 4-hydroxycoumarin and malononitrile. In solvent-free condition, the related product was obtained with the best yield (Table 1, entries 3 and 6). The reactions in ethyl acetate afforded very poor yields whilst using the mentioned NIL in *n*-hexane and toluene could not effectively catalyze the reaction. The effect of catalyst loading was also examined (Table 1, entries 3-16). It was found that 0.5 mol% of NIL catalyst was sufficient to proceed the reaction to completion and a 91% yield was obtained (Table 1, entry 3). Higher amounts of the catalyst provided the same results. Finally, the effect of temperature on the rate of the reaction was studied (Table 1, Entries 1-9). It was found that the reaction at room temperature gave the best yield (Table 1, Entries 3 and 6).

[a]Reaction condition: 4-Nitrobenzaldehyde (1 mmol; 0.151 g), 4-hydroxycoumarin (1 mmol; 0.162 g), malononitrile (1.2 mmol; 0.079 g);

Table 1. Optimizing the reaction condition in the synthesis of 3,4-dihydropyrano[*c*]chromenes.[a]

Entry	Catalyst amount (mol%)	Solvent	Temperature (°C)	Time (min)	Yield[b] (%)
1	—	Solvent-free	r.t.	60	Trace
2	—	Solvent-free	100	50	Trace
3	0.5	Solvent-free	r.t.	10	91
4	0.5	Solvent-free	50	10	91
5	0.5	Solvent-free	100	10	91
6	1	Solvent-free	r.t.	10	91
7	1	Solvent-free	100	10	91
8	2	Solvent-free	r.t.	10	87
9	2	Solvent-free	100	10	87
10	0.5	Ethyl acetate	r.t.	30	38
11	0.5	C_2H_5OH	r.t.	15	87
12	0.5	CH_3CN	r.t.	25	82
13	0.5	CH_3OH	r.t.	15	86
14	0.5	CH_2Cl_2	r.t.	12	86
15	0.5	*n*-Hexane	r.t.	10	63
16	0.5	Toluene	r.t.	20	65

[a]Reaction condition: 4-Nitrobenzaldehyde (1 mmol; 0.151 g), 4-hydroxycoumarin (1 mmol; 0.162 g), malononitrile (1.2 mmol; 0.079 g)
[b]Isolated yield.

Table 2. Synthesis of 3,4-dihydropyrano[*c*]chromenes using {[2,2'-BPyH][C(CN)$_3$]$_2$}.[a]

Entry	Aldehyde	Time (min)	Yield[b] (%)	M.p. (°C) [Lit.] (Color) Ref.
1	4-Nitrobenzaldehyde	10	91	269-271 [258-260] (Yellow) [43]
2	4-Chlorobenzaldehyde	12	90	270-272 [256-258] (White) [29]
3	3-Nitrobenzaldehyde	12	89	270-272 [262-264] (White) [43]
4	2-Chlorobenzaldehyde	15	89	268-270 [266-268] (White) [44]
5	4-Dimethylaminobenzaldehyde	18	89	265-267 [2665-267] (Yellow) [29]
6	2-Methoxybenzaldehyde	20	88	248-250 [274-276] (White) [45]
7	4-Methylbenzaldehyde	15	87	254-256 [259-260] (White) [43]
8	4-Hydroxybenzaldehyde	15	85	261-263 [260-263] (White) [43]
9	3-Hydroxybenzaldehyde	18	84	248-250 [269-270] (White) [43]
10	4-Flourobenzaldehyde	15	91	259-261 [260-262] (White) [29]
11	Thiophene-2-carbaldehyde	15	83	245-247 [245-247] (White) [16]
12	Furfural	15	83	224-226 [223-225] (Cream) [16]
13	Cinnamaldehyde	20	82	188-190 [187-189] (Yellow) [19]
14	Benzaldehyde	20	87	245-247 [256-258] (White) [43]

[a]Reaction condition: Aldehyde (1 mmol), 4-hydroxycoumarin (1 mmol; 0.162 g), malononitrile (1.2 mmol; 0.079 g), {[2,2'-BPyH][C(CN)$_3$]$_2$} (0.5 mol%; 0.0017 g), solvent-free, r.t.; [b]Isolated yield.

[b]Isolated yield.

The scope and limitations of the reaction were examined under the optimized conditions. It was realized that this process is appropriate to a wide range of aromatic aldehydes including electron-withdrawing and electron-donating groups, providing an easy access to 3,4-dihydropyrano[*c*]chromenes with good to excellent yields. The results are summarized in Table 2.

The reusability of the catalyst is a significant indicator from environmental points of view. For this reason, the reusability of {[2,2'-BPyH][C(CN)$_3$]$_2$} was examined in the reaction of 4-nitrobenzaldehyde, 4-hydroxycoumarin and malononitrile under the optimized reaction condition. It was found that the NIL catalyst could be reused five times and the products were attained in 91, 91, 90, 89 and 87% yield respectively.

A possible mechanism for the synthesis of 3,4-dihydropyrano[*c*]chromene (**4**) was displayed in Scheme 2 [10-26]. Firstly, {[2,2'-BPyH][C(CN)$_3$]$_2$} activates the carbonyl group of aldehyde (1) and malononitrile (**3**). The Knoevenagel condensation of (**2**) and (**3**) was occurred to form the arylidene malononitrile (**6**). Then, 4-hydroxycoumarin (**1**) tolerates nucleophilic attack to (**6**) giving the Michael addition adduct (**7**). The Michael adduct (**7**) is cyclized to provide compound (**8**) and then tautomerized to afford the fully conjugated 3,4-dihydropyrano[*c*]chromene (**4**).

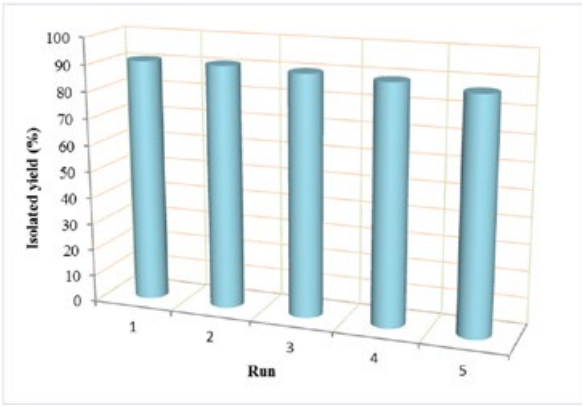
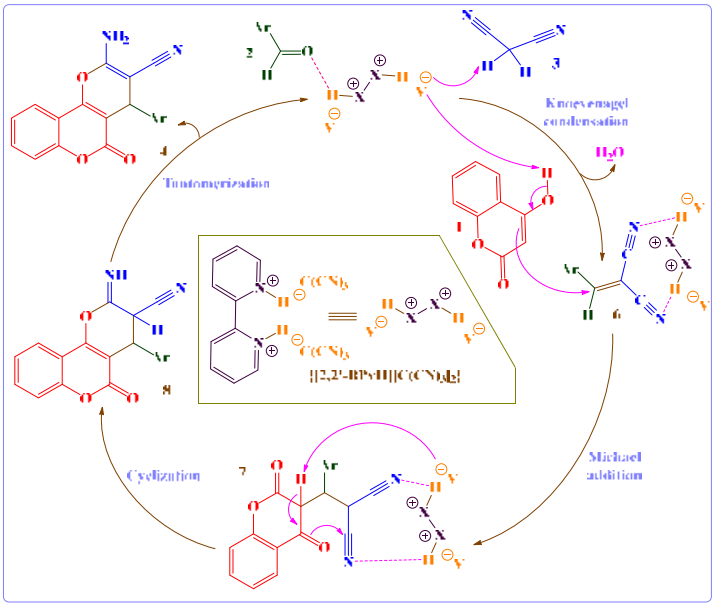


Fig. 1. Reusability of {[2,2'-BPyH][C(CN)$_3$]$_2$} in the synthesis of 3,4-dihydropyrano[*c*]chromene for the model reaction in 10 min.



Scheme 2. Proposed mechanism for the synthesis of 3,4-dihydropyrano[*c*]chromenes using {[2,2'-BPyH][C(CN)$_3$]$_2$}.

Application of {[2,2'-BPyH][C(CN)$_3$]$_2$} as a NIL catalyst for the synthesis of biscoumarins.

In order to optimize the reaction condition, different experimental parameters were investigated . As seen from Table 3, 0.5 mol% of NIL catalyst was found to be the optimum amount (Table 3, entries 3-5). There was no important change in the yield of products when larger amounts of NIL catalyst were used (Table 3, entries 6-9). The effect of temperature was studied by performing the model reaction at room temperature, 50 °C and 100 °C. The best result was attained at room temperature (Table 3, entry 3). Finally, reaction was examined in common organic solvents with varying polarities

Table 3. Optimizing the reaction condition in the synthesis of biscoumarins.[a]

Entry	Catalyst amount (mol%)	Solvent	Temperature (°C)	Time (min)	Yield[b] (%)
1	—	Solvent-free	r.t.	60	8
2	—	Solvent-free	100	60	7
3	0.5	Solvent-free	r.t.	10	91
4	0.5	Solvent-free	50	10	91
5	0.5	Solvent-free	100	10	91
6	1	Solvent-free	r.t.	10	91
7	1	Solvent-free	100	10	91
8	2	Solvent-free	r.t.	10	88
9	2	Solvent-free	100	10	88
10	0.5	C_2H_5OH	r.t.	20	88
11	0.5	CH_3OH	r.t.	25	88
12	0.5	CH_2Cl_2	r.t.	20	86
13	0.5	*n*-Hexane	r.t.	20	60
14	0.5	Toluene	r.t.	30	68

[a]Reaction condition: 4-Nitrobenzaldehyde (1 mmol; 0.151 g), 4-hydroxycoumarin (2 mmol; 0.324 g); [b]Isolated yield.

Table 4. Synthesis of biscoumarins using {[2,2'-BPyH][C(CN)$_3$]$_2$}.[a]

Entry	Aldehyde	Time (min)	Yield[b] (%)	M.p. (°C) [Lit.] (Color) Ref.
1	4-Nitrobenzaldehyde	10	91	234-236 [232-234] (White) [43]
2	4-Chlorobenzaldehyde	10	92	260-262 [257-259] (White) [43]
3	4-Hydroxybenzaldehyde	20	87	228-230 [228-230] (Yellow) [43]
4	3-Nitrobenzaldehyde	12	90	233-235 [212-215] (White) [43]
5	2-Chlorobenzaldehyde	12	90	270-272 [224-226] (White) [46]
6	4-Dimethylaminobenzaldehyde	15	90	219-221 [222-224] (Pink) [29]
7	4-Methylbenzaldehyde	10	90	264-266 [269-270] (White) [43]
8	Furfural	15	88	194-196 [200-202] (Brown) [46]

[a]Reaction condition: Aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol; 0.324 g), {[2,2'-BPyH][C(CN)$_3$]$_2$} (0.5 mol%; 0.0017 g), solvent-free, r.t.; [b]Isolated yield.

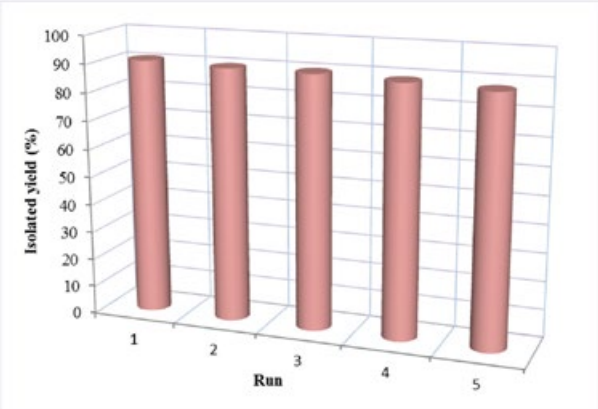


Fig. 2. Reusability of {[2,2'-BPyH][C(CN)$_3$]$_2$} in the synthesis of biscoumarin for the model reaction in 10 min.

(Table 3, entries 10-14).

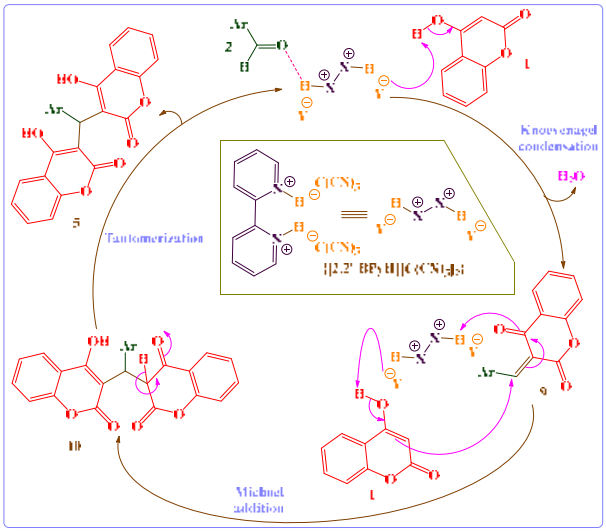
To evaluate the efficacy and scope, 4-hydroxycoumarin was reacted with several aldehydes. The results are presented in Table 4, showing that all reactions proceeded efficiently, and the desired products were produced at high yield and short reaction time. The effect of electron-withdrawing substituents, electron-releasing substituents and halogens on the aromatic ring of aldehydes on the reaction results was studied. As seen in Table 4, electron-withdrawing substituents and halogens had no significant effect on the yield and reaction time. However, electron-releasing groups slightly decreased the yield and increased the reaction time.

The recyclability of the catalyst in the reaction of 4-nitrobenzaldehyde and 4-hydroxycoumarin in the presence of {[2,2'-BPyH][C(CN)$_3$]$_2$} was examined (Fig. 2). The separated catalyst was used in the revealed reaction 5 times and the products were obtained in 91, 90, 90, 89 and 88% yield, respectively.

A proposed mechanism for the synthesis of biscoumarins is shown in Scheme 3 [33-40]. Firstly {[2,2'-BPyH][C(CN)$_3$]$_2$} activates the carbonyl group of the aromatic aldehyde (**2**). Then, Knoevenagel condensation occurred by nucleophilic attack of activated 4-hydroxycoumarin (**1**) to activate aldehyde (**2**) and reaction followed *via* elimination of one H_2O molecule formed in intermediate (**9**). Then, NIL catalyst activates the carbonyl group of the intermediate (**9**) and nucleophilic attack of the second equivalent of activated 4-hydroxycoumarin (**1**) by Michael addition produces *α,β*-unsaturated ketone (intermediate **10**). In the final step intermediate

Table 5. Comparison of the results of the condensation reaction of 4-chlorobenzaldehyde with 4-hydroxycoumarin catalyzed by {[2,2'-BPyH][C(CN)$_3$]$_2$} with those attained by the reported catalysts.

Entry	Reaction condition	Amount of catalyst	Time (min)	Yield (%)	[Ref.]
1	{[2,2'-BPyH][C(CN)$_3$]$_2$}, Solvent-free, r.t.	0.5 mol%	10	92	This work
2	TBAB, H_2O, 100 °C	10 mol%	30	95	[12]
3	TBAB, Solvent-free, 100 °C	10 mol%	20	87	[12]
4	[MIM(CH$_2$)$_4$SO$_3$H][HSO$_4$], Solvent-free, 80 °C	15 mol%	25	93	[47]
5	Catalyst-free, microwave (time: 5 min; power: 75%), C_2H_5OH	—	300	35	[29]
6	Catalyst-free, microwave (time: 5 min; power: 75%), silica-gel supported	—	300	87	[29]
7	Catalyst-free, conventional (Δ)	—	300	84	[29]
8	SDS, H_2O, 60 °C	20 mol%	150	93	[29]
9	{Fe_3O_4@SiO_2@(CH$_2$)$_3$Semicarbazide-SO_3H/Cl} MNPs, Solvent-free, 80 °C	10 mg	20	80	[34]



Scheme 3. Proposed mechanism for the synthesis of biscoumarins using {[2,2'-BPyH][C(CN)$_3$]$_2$}.

(**10**) was tautomerized to its corresponding biscoumarin (**5**).

The efficiency of {[2,2'-BPyH][C(CN)$_3$]$_2$} as a catalyst in the synthesis of biscoumarins was investigated in comparison with some other catalysts. To this end, the reaction of 4-chlorobenzaldehyde with 4-hydroxycoumarin was studied in the presence of these catalysts (Table 5). As revealed in Table 5, the synthesis of biscoumarins using {[2,2'-BPyH][C(CN)$_3$]$_2$} as a catalyst was resulted in the best results for this reaction.

CONCLUSION

We have described a convenient methodology for the synthesis of 3,4-dihydropyrano[*c*]chromene and biscoumarin in the presence of {[2,2'-BPyH][C(CN)$_3$]$_2$} as a recyclable and efficient NIL catalyst (0.5 mol%) under solvent-free condition at room temperature in high yield and short reaction time. The major advantages of the presented methodology are simplicity provided, operational simplicity and green process avoiding hazardous organic solvents.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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