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ARTICLE

Synthesis of a novel bifunctional oxyammonium-based ionic liquid: Application for the synthesis of pyrano[4,3-*b*] pyrans and tetrahydrobenzo[*b*]pyrans

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Abstract

In the present investigation, a novel bifunctional oxyammonium-based ionic liquid, namely, 2,2′-(ethane-1,2-diylbis[oxy])bis(ethan-1-aminium)-2,2,2-trifluoroacetate, was designed and synthesized. The structure of the titled ionic liquid was characterized using Fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^{1}HNMR), carbon nuclear magnetic resonance (^{13}CNMR), fluorine nuclear magnetic resonance (^{19}FNMR), homonuclear COSY nuclear magnetic resonance (NMR), thermogravimetry (TG), derivative thermogravimetry (DTG) analysis, X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The described ionic liquid demonstrated robust catalytic performance in the synthesis of pyrano[4,3-b]pyrans and tetrahydrobenzo[b]pyran derivatives. The ionic liquid presents a high potential of recycling and reusing capability in both types of model reactions.

KEYWORDS

bifunctional ionic liquid, multicomponent reactions, oxyammonium-based ionic liquid, pyrano[4,3-*b*]pyrans, tetrahydrobenzo[*b*]pyrans

1 | INTRODUCTION

Over the routine, step-by-step sequential access to highly valuable and complex structures, a one-pot multicomponent method provides several conceptual and synthetical merits. The privileged advantages of one-pot multicomponent reactions are due to the rapid achievement of complexity and diversity in organic synthesis through high practical and time-saving approaches. In addition, this synthetic tool allows the chemists to meet the criteria of green chemistry, such as atom and step economy, waste prevention, saving of solvents and reagents, avoidance of hazardous materials, uncomplicated purification procedures, and energy efficiency.[1–8]

Due to the presence of bulky and asymmetric ions within the structure of ionic liquids, they melt at temperatures lower than 100°C. Frequently, ionic liquids are referred to as tunable, tailored, task-specific, or designable species. This is because the properties of ionic liquids can be easily adjusted by the discreet selection of suitable anions and cations. Currently, due to remarkable typical characteristics such as minor vapor pressure, large temperature window of molten state, excellent solvation properties, high chemical and thermal stability, lack of inflammability, wide electrochemical window, and respectable ion conductivity, ionic liquids emerged as an interdisciplinary area and found a critical rule in different fields of science. Compared with bulky ionic liquids, nanoionic

liquids have been able to overcome disadvantages such as high cost and viscosity and slow gas diffusivity. Hence, novel task-specific ionic liquids for resolving the above-mentioned drawbacks are more in demand.[9–17]

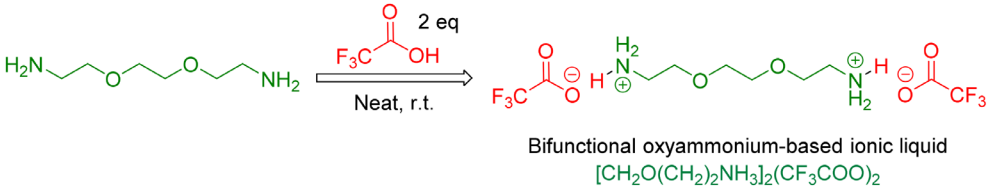
Among the biological active heterocyclic compounds, 4*H*-pyran structural motifs have a vital position in many natural products and drugs and represent varied pharmacological properties. For example, (4-oxo-4*H*-pyran-2-yl) acrylic acid esters are used as tyrosinase inhibitors,[18] 4-phenyl-4*H*-pyrans are IKCa channel blockers,[19] and 2-amino-4*H*-pyrans are applied as an antibacterial.[20] Fused 4*H*-pyran derivatives, such as pyrano[4,3-*b*]pyran derivatives, have been widely used in various molecules exhibiting a broad range of pharmacological applications, such as antiviral,[21] anticonvulsant and antimicrobial,[22] antileishmanial,[23] antiproliferative,[24] antiviral,[25] anti-HIV, antituberculosis, and antifungal agents.[26] Therefore, it is expected that the preparation of these versatile compounds is an important goal for chemists. Some previously reported methods for the synthesis of pyrano[4,3-*b*] pyrans include using catalysts such as KF-Al_2O_3,[27] triethylbenzyl ammonium chloride,[28] piperidine[29] and NH_4OAc[30] magnesium oxide,[31] DBU,[32] $H_6P2W_{18}O_{62}{\cdot}18H_2O$,[33] nanoeggshell/$Cu(OH)_2$,[34] thiourea dioxide,[35] 4-(Succinimido)-1-butane sulfonic acid,[36] nano-CaO,[37] $[BBMIm](HSO_4)_2$,[38] electrocatalysis,[39] alum[40] [18-C-6 K][OAc][41] DABCO,[42] PNO/Ag_2O,[43] $(CTA)_3[SiW_{14}]$-Li^+-MMT,[44] and sodium ethylene diamine tetraacetate.[45]

As in the case of pyrano[4,3-*b*]pyran derivatives, tetrahydrobenzo[*b*]pyrans are privileged heterocyclic structures that represent the varied scope of pharmaceutical and biological applications. These types of heterocyclic structures have been applied in the treatment of neurodegenerative diseases, such as Alzheimer's, Huntington's, Parkinson's, and Down's syndrome and also in the treatment of myoclonus and schizophrenia.[46,47] Tetrahydrobenzo[*b*]pyran derivatives have been used as for diuretic, anticancer, and antianaphylactic activities and as anticoagulant agents.[48–51] In the last few years, owing to the above-mentioned versatilities of tetrahydrobenzo[*b*]pyrans, various efforts have been made to present new procedures for their construction.[52–75]

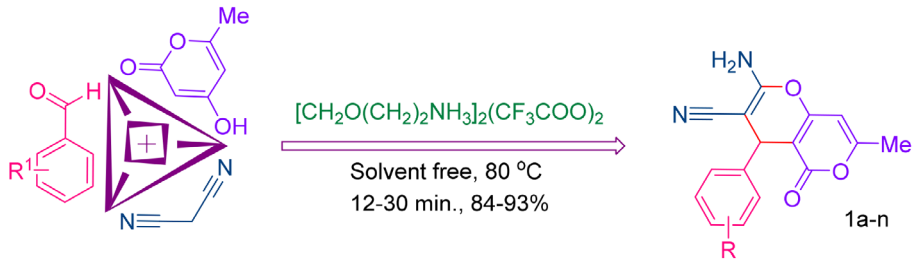
In the present work, keeping in mind the usefulness and efficiency of ionic liquids and the biological importance of pyrano[4,3-*b*]pyrans and tetrahydrobenzo[*b*] pyran derivatives and following our earlier efforts of the knowledge-based development of task-specific catalysts for the preparation of valuable heterocyclic compounds,[76–91] we wish to report the design, synthesis, and catalytic application of a novel bifunctional oxyammonium-based ionic liquid $[CH_2O(CH_2)_2NH_3]_2(CF_3COO)_2$ toward the synthesis of pyrano[4,3-b]pyrans and tetrahydrobenzo[*b*]pyrans under mild reaction conditions (Schemes 1–3).

2 | RESULTS AND DISCUSSION

The design, synthesis, and application of multifunctional hydrophilic ionic liquids are our main focus. With this aim, we have applied an open-chain amine with glycolic spacers as a suitable starting material for the synthesis of desired ionic liquid. The bifunctional oxyammonium-based ionic liquid $[CH_2O(CH_2)_2NH_3]_2(CF_3COO)_2$ was synthesized via a simple procedure. The described ionic liquids were fully characterized by using various technical methods, such as Fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^{1}HNMR), carbon

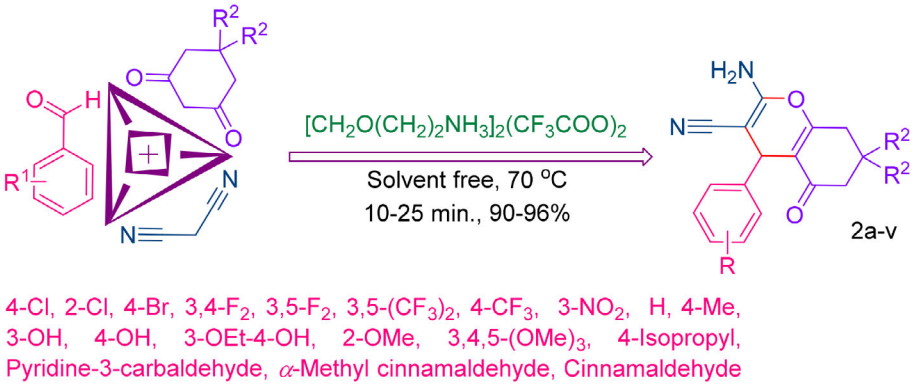


SCHEME 1 Preparation of bifunctional oxyammonium-based ionic liquid

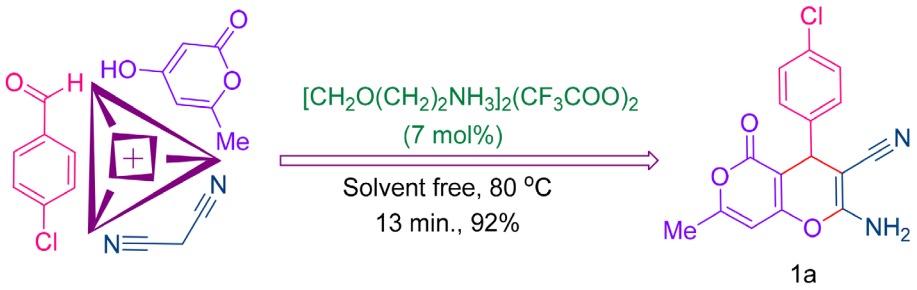


SCHEME 2 Synthesis of pyrano [4,3-*b*]pyrans in the presence of $[CH_2O(CH_2)_2NH_3]_2(CF_3COO)_2$

SCHEME 3 Synthesis of tetrahydrobenzo[*b*]pyrans in the presence of $[CH_2O(CH_2)_2NH_3]_2(CF_3COO)_2$



SCHEME 4 Optimal reaction condition for the synthesis of target molecule **1a**



nuclear magnetic resonance (^{13}CNMR), fluorine nuclear magnetic resonance (^{19}FNMR), homonuclear COSY nuclear magnetic resonance (NMR), thermogravimetry (TG), derivative thermogravimetry (DTG), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). All of the used methods confirmed the successful synthesis of the titled catalyst. Details are discussed in the electronic supporting information.

2.1 | Catalytic performance of the novel ionic liquid in multicomponent reactions

After verification of the formation of the titled ionic liquid catalyst using the above-discussed methods, due to the pharmaceutical versatilities of the pyrano[4,3-*b*]pyrans and tetrahydrobenzo[*b*]pyrans, we were encouraged to study the catalytic activity of the described ionic liquid toward the synthesis of these heterocyclic scaffolds.

In an initial endeavor, in the case of pyrano[4,3-*b*]pyrans, the reaction between equivalent amounts of 4-chlorobenzaldehyde, malononitrile, and 4-hydroxy-6-methyl-2*H*-pyran-2-one was selected as a test reaction (Scheme 4). Using model reaction, effective reaction parameters, including solvents, the load of catalyst, and operational reaction temperature, were checked thoroughly. With respect to the reaction time and yield of the desired compound under different conditions, the outcome data imply that a solvent-free condition at 80°C in the presence of 7 mol% of ionic liquid catalyst (Table 1, Entry 10) is the optimal reaction condition. The related data are presented in Table 1.

After determination of the optimal reaction parameters for the synthesis of target molecule **1a**, aromatic aldehydes bearing either electron-withdrawing or electron-donating substituents were tested using the optimal reaction conditions to yield the desired molecules **1a–n**. From the achieved experimental results, the reactions for all substrates were found to proceed smoothly toward the desired pyrano[4,3-*b*]pyran derivatives in short reaction times with excellent yields (Scheme 2 and Table 2).

The promising obtained result from the catalytic application of ionic liquid encouraged us to test its catalytic performance in the synthesis of tetrahydrobenzo[*b*]pyrans as biological active target structures. In the case of tetrahydrobenzo[*b*]pyrans, the best reaction condition scrutinized over the reaction of 4-chlorobenzaldehyde, malononitrile and dimedone (Scheme 5). Respect to green nature, reaction time and yield of the desired molecule 2a, the best experimental data were obtained in the presence of 7 mol% of ionic liquid at 70 °C undersolvent-free condition (Table 3, Entry 8).

Afterward, as in the case of pyrano[4,3-*b*]pyrans, the generality and scope of the presented method was investigated regarding the green synthesis of tetrahydrobenzo[*b*]pyran derivatives. For this goal, with optimal reaction conditions in hand, the varied aromatic aldehyde with electron-withdrawing and electron-releasing groups was

TABLE 1 Optimization of reaction conditions for the synthesis of desired molecule **1a**[a]

Entry	Solvent	Load of catalyst (mol%)	Temperature (°C)	Time (min.)	Yield (%)[b]
1	—	10	r.t.	240	—
2	—	10	50	60	80
3	—	10	60	20	87
4	—	10	70	18	90
5	—	10	80	13	93
6	—	10	90	13	93
7	—	5	80	25	88
8	—	3	80	30	85
9	—	—	80	300	—
10	**—**	**7**	**80**	**13**	**92**
11	EtOH	7	80	30	90
12	H_2O	7	80	35	87
13	CH_3CN	7	80	100	85
14	*n*-hexane	7	80	80	83
15	EtOAc	7	80	80	60
16	THF	7	80	90	80

Note: The bold values represent optimized reaction conditions.
[a]*Reaction conditions*: 4-chlorobenzaldehyde (1 mmol, 0.140 g), malononitrile (1 mmol, 0.066 g), 4-hydroxy-6-methyl-2*H*-pyran- 2-one (1 mmol, 0.126 g).
[b]Isolated yield.

TABLE 2 Synthesis of target molecules 1a–n in the presence of novel bifunctional oxyammonium-based ionic liquid catalyst[a]

Entry	Product	R	Time (min)	Yield (%)[b]	Melting point (°C), found [lit.][ref.]
1	**1a**	4-cl	13	92	219–222 [220–222][77]
2	**1b**	4-me	18	88	226–228 [207–209][77]
3	**1c**	H	15	85	246–248 [250–252][77]
4	**1d**	3-NO_2	20	89	228–230 [232–234][77]
5	**1e**	Pyridine-3-carbaldehyde	12	93	215–217 [222–224][41]
6	**1f**	2-OMe	25	85	240–244 [243–245][41]
7	**1g**	α-Methyl cinnamaldehyde	25	86	178–180 [new]
8	**1h**	4-Br	15	92	219–221[212–215][77]
9	**1i**	4-OH	30	84	238–240 [not reported][34]
10	**1j**	2-cl	17	91	258–260 [262–264][77]
11	**1k**	3,4,5-$(OMe)_3$	30	87	227–229 [not reported][42]
12	**1l**	3,5-F_2	18	93	244–246 [new]
13	**1m**	3,5-$(CF_3)_2$	20	91	248–250 [new]
14	**1n**	4-isopropyl	25	84	225–227 [new]

[a]*Reaction conditions*: aryldehyde (1 mmol), malononitrile (1 mmol, 0.066 g), 4-hydroxy-6-methyl-2*H*-pyran- 2-one (1 mmol, 0.126 g).
[b]Isolated yields.

subjected to the reaction with malononitrile and dimedone or cyclohexane-1,3-dione. The achieved experimental data for the synthesis of tetrahydrobenzo[*b*]pyrans were collected in Table 4. All the reactions can lead to the desired molecules in short reaction times with excellent yields (Scheme 3, Table 4).

A typical plausible mechanistic process for the synthesis of the desired compound **1b** is illustrated in Scheme 6. The dual-role ionic liquid catalyst simultaneously activates both benzaldehyde and malononitrile to initiate the mechanistic process. A nucleophilic attack from malononitrile on activated benzaldehyde yields

SCHEME 5 Optimal reaction condition for the synthesis of target molecule **2a**

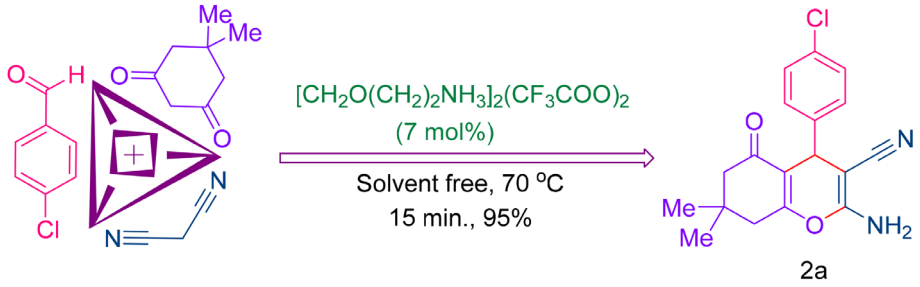


TABLE 3 Optimization of reaction conditions for the synthesis of desired molecule **2a**[a]

Entry	Solvent	Load of catalyst (mol%)	Temperature (°C)	Time (min)	Yield (%)[b]
1	—	10	r.t.	120	80
2	—	10	50	60	87
3	—	10	70	15	95
4	—	10	80	15	95
5	—	5	70	25	88
6	—	3	70	35	80
7	—	—	70	240	60
8	**—**	**7**	**70**	**15**	**95**
9	EtOH	7	70	25	93
10	H_2O	7	70	30	87
11	CH_3CN	7	70	90	87
12	*n*-hexane	7	70	60	83
13	EtOAc	7	70	60	60
14	THF	7	70	60	90

[a]*Reaction conditions*: 4-chlorobenzaldehyde (1 mmol, 0.140 g), malononitrile (1 mmol, 0.066 g), dimedone (1 mmol, 0.140 g).
[b]Isolated yield.

Knoevenagel intermediate **2** after dehydration. In the next step, the Knoevenagel intermediate **2** acts as a Michael acceptor and is subjected to the reaction with the activated 4-hydroxy-6-methyl-2*H*-pyran-2-one, which produces the intermediate **3**. Afterward, intermediate **4** formed from an intramolecular nucleophilic attack by the oxygen atom on the nitrile group. In the presence of the catalyst, this intermediate tautomerized to the desired molecule **1b**.

In the case of tetrahydrobenzo[*b*]pyran derivatives, compound **2b** was selected as a model, and the suggested mechanism is as depicted in Scheme 7. Similar to a plausible mechanism for compound **1b**, in the presence of ionic liquid catalyst, Knoevenagel intermediate **2** was generated from the reaction of benzaldehyde and malononitrile. This intermediate is exposed to a nucleophilic attack from the enol form of dimedone. This reaction generates intermediate **5,** which undergoes an intramolecular nucleophilic attack to yield the corresponding intermediate **6**. Finally, the desired product **2b** was obtained using a tautomerization process in the presence of catalyst (Scheme 7).

2.2 | Recyclability of the novel ionic liquid

In another investigation, catalyst recovery and reuse as a very important issue from the viewpoint of green chemistry principals were inspected in both types of multicomponent reactions. The results were quite satisfactory. After completion of each run, to separate the catalyst, 5 ml of distillated water was added to the reaction mixture and stirred for 5 min. The ionic liquid catalyst was dissolved in distillated water, while the product and unreacted starting materials did not dissolve. Through simple filtration and evaporation of the solvent, the catalyst was recovered and preserved for the next run. The recovered ionic liquid catalyst could be reused for three runs in both cases of the reactions. In both cases of the multicomponent reactions, the recovery

TABLE 4 Synthesis of target molecules 2a–v in the presence of novel bifunctional oxyammonium-based ionic liquid catalyst[a]

Entry	Product	R^1	R^2	Time (min)	Yield (%)[b]	Melting point (°C), found [lit.][ref.]
1	**2a**	4-cl	Me	15	95	192–202 [210–212][82]
2	**2b**	4-me	Me	20	90	219–223 [215–217][82]
3	**2c**	H	Me	20	92	187–190 [227–229][82]
4	**2d**	4-OMe	Me	18	92	190–194 [195–197][82]
5	**2e**	2-cl	Me	15	94	191–202 [212–214][82]
6	**2f**	4-Br	Me	15	93	197–201 [205–207][82]
7	**2g**	4-NO_2	Me	18	95	174–177 [180–182][82]
8	**2h**	4-isopropyl	Me	20	90	203–207 [196–197][74]
9	**2i**	3-OEt-4-OH	Me	22	91	219–222 [218–220][75]
10	**2j**	3-OH	Me	25	90	229–232 [205–206][69]
11	**2k**	Cinnamaldehyde	Me	15	95	185–188 [215–218][71]
12	**2l**	3-NO_2	Me	15	96	209–213 [211–213][82]
13	**2m**	Pyridine-3-carboxaldehyde	Me	10	96	184–187 [255–256][70]
14	**2n**	α-Methyl cinnamaldehyde	Me	18	93	204–207 [207–209][67]
15	**2o**	2-OMe	Me	20	90	198–202 [203–205][68]
16	**2p**	3,5-F_2	Me	15	93	225–227 [new]
17	**2q**	4-CF_3	Me	16	94	217–219 [218–219][69]
18	**2r**	3,5-$(CF_3)_2$	Me	18	91	232–236 [169–170][73]
19	**2s**	3,4-F_2	Me	12	93	184–188 [new]
20	**2t**	3,5-F_2	H	13	92	239–241 [250–252][72]
21	**2u**	4-CF_3	H	15	93	209–212 [210–212][72]
22	**2v**	3,5-$(CF_3)_2$	H	20	90	256–259 [new]

[a]*Reaction conditions*: aryldehyde (1 mmol), malononitrile (1 mmol, 0.066 g), dimedone or cyclohexane-1,3-dione (1 mmol).
[b]Isolated yield.

and reusability test was examined over the reaction of 4-chlorobenzaldehyde, malononitrile, and 4-hydroxy-6-methyl-2*H*pyran-2-one or dimedone in the related optimal reaction conditions as depicted in Scheme 8.

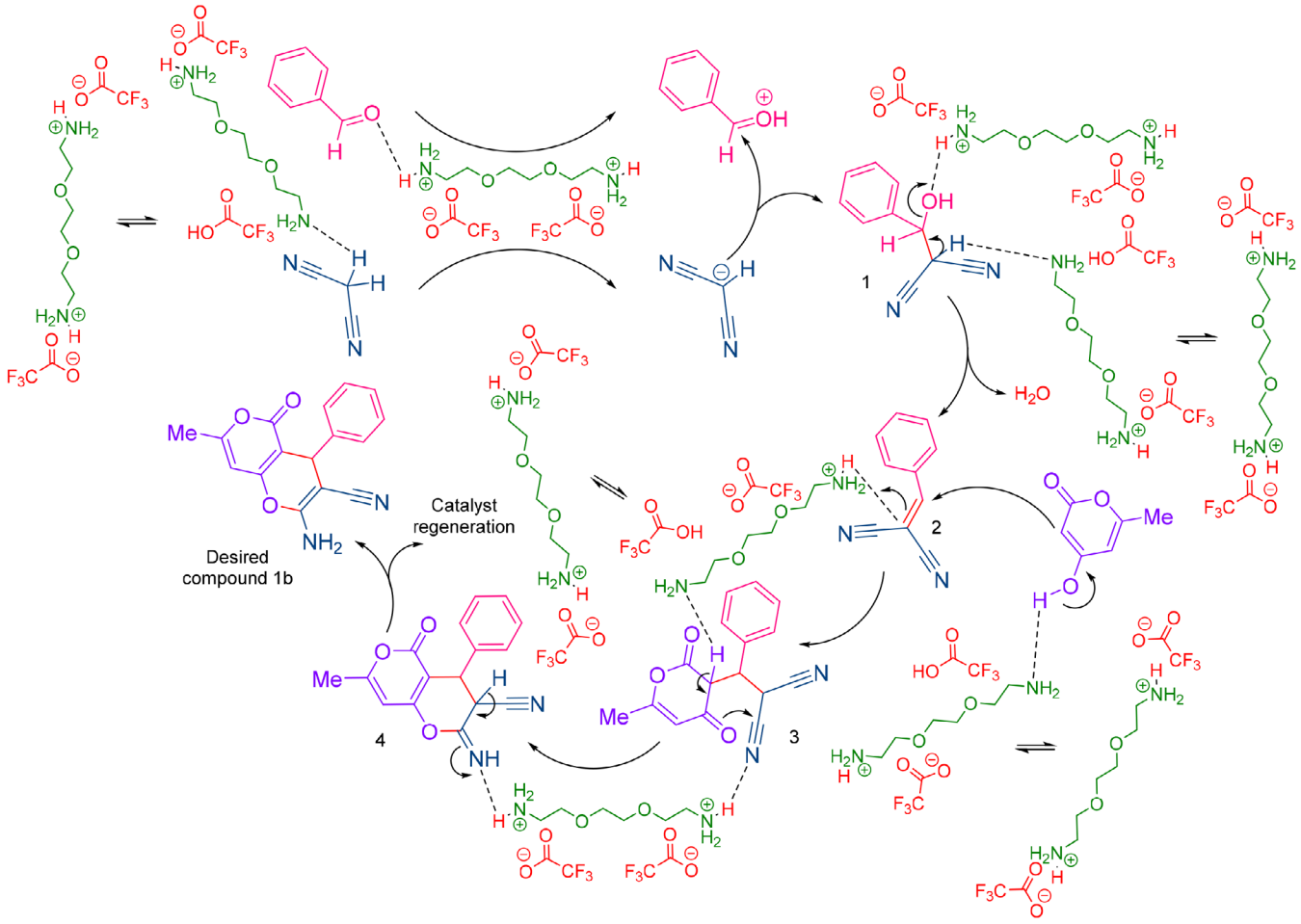
3 | EXPERIMENTAL

3.1 | General method for the synthesis of novel bifunctional ionic liquid catalyst

The novel bifunctional oxyammonium-based ionic liquid catalyst was synthesized as follows: 10 mmol (1.14 g, 0.77 ml) of trifluoracetic acid was added dropwise to a round-bottom flask containing 5 mmol (0.74 g, 0.73 ml) of 1,8-diamino-3,6-dioxaoctane under neat conditions at ambient temperature. During the addition of acid to base, the mixture was stirred vigorously. After the addition was completed, the mixture was stirred for 2 hr. The obtained thick precipitate was washed thoroughly with diethyl ether (3 × 10 ml) to afford a pure ionic liquid catalyst as desired product. All obtained data confirmed the successful formation of the catalyst.

3.2 | General method for the synthesis of pyrano[4,3-*b*]pyrans in the presence of novel bifunctional ionic liquid catalyst

At the optimal reaction conditions depicted in Table 1 (solvent free, 80°C, 7 mol% of ionic liquid), a mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol, 0.066 g), and 4-hydroxy-6-methyl-2*H*-pyran-2-one (1 mmol, 0.126 g) was subjected to the reaction for proper times as given in Table 2. After completion of the reaction as monitored by TLC, in order to separate the ionic liquid catalyst, 5 ml of distillated water was added to the mixture and stirred for 5 min. The catalyst was removed from the reaction mixture by simple filtration. Through evaporation of the solvent, the catalyst was recovered and preserved for



SCHEME 6 A plausible mechanism for the synthesis of desired compound **1b**

the next run. The filtrated crude product was washed with hot ethanol and air dried to yield the desired molecules.

3.3 | General method for the synthesis of tetrahydrobenzo[*b*]pyrans in the presence of novel bifunctional ionic liquid catalyst

At 70°C, 7 mol% of ionic liquid was added to a round-bottom flask containing a mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol, 0.066 g), and dimedone or cyclohexane-1,3-dione (1 mmol) as a catalyst. The resulting mixture was stirred for the appropriate times as given in Table 4. The progress of the reaction was monitored by TLC. After completion of the reaction, water (5 ml) was added to the reaction mixture, and the catalyst was removed from the reaction mixture and recovered for the next run. The reaction mixture was filtered, and residue was purified by washing with hot ethanol and air dried to yield the desired structures.

3.4 | Selected spectral data

3.4.1 | Spectral data of the bifunctional oxyammonium-based ionic liquid

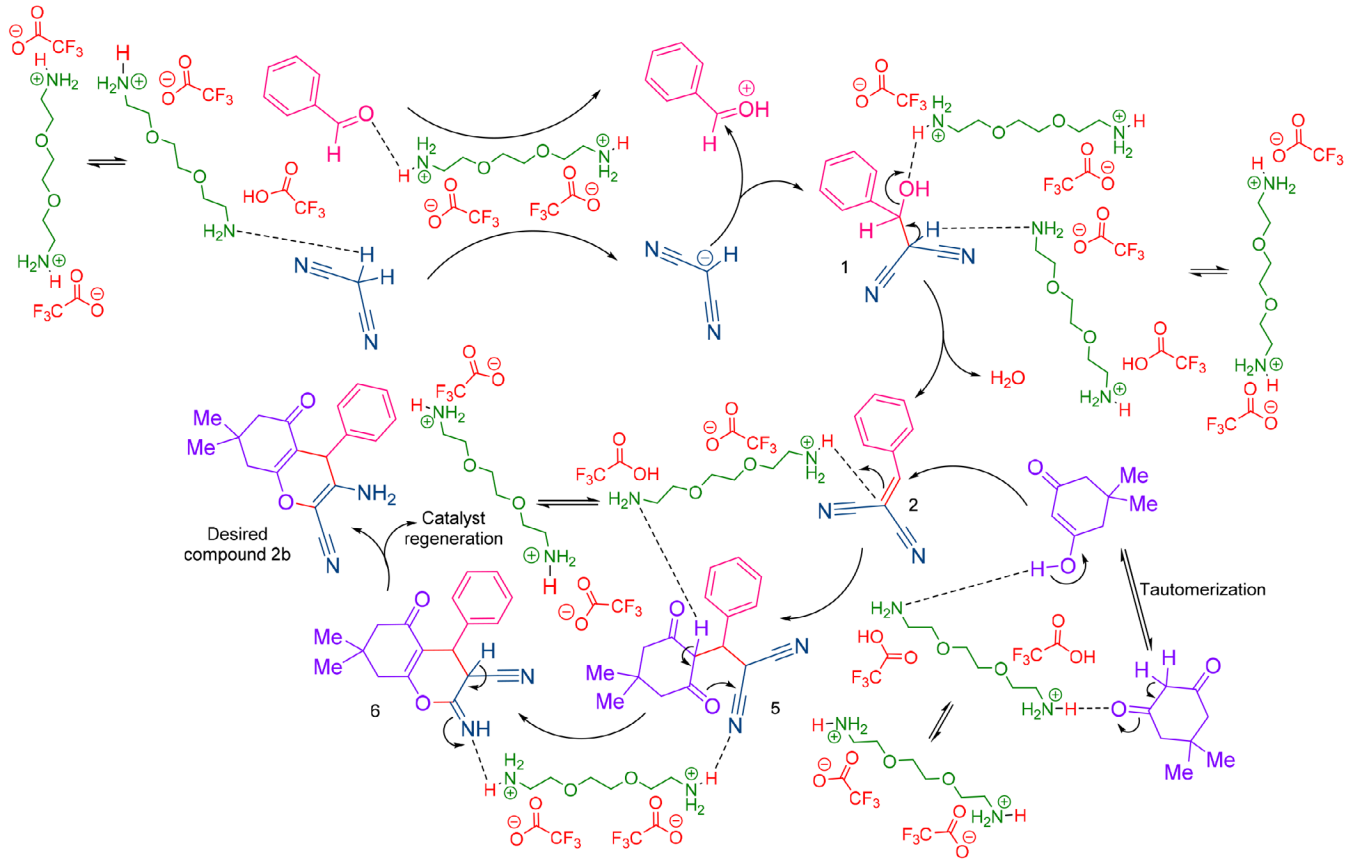
2,2′-(Ethane-1,2-diylbis[oxy])bis(Ethan-1-aminium) 2,2,2-trifluoroacetate

Melting point: 90–92°C; ^{1}H NMR (300 MHz): δ_{ppm} 8.03 (bs, 6H, NH), 3.61 (t, J = 3 Hz, 4H, CH_2), 3.58 (s, 4H, CH_2), 2.98 (t, J = 3 Hz, 4H, CH_2); ^{13}C NMR (75 MHz): δ_{ppm} 158.6 (q, J = 23.3 Hz, C=O), 117.1 (q, J = 222.7 Hz, CF_3), 69.4, 66.6, 38.5, ^{19}F NMR (282 MHz): δ_{ppm} − 73.8.

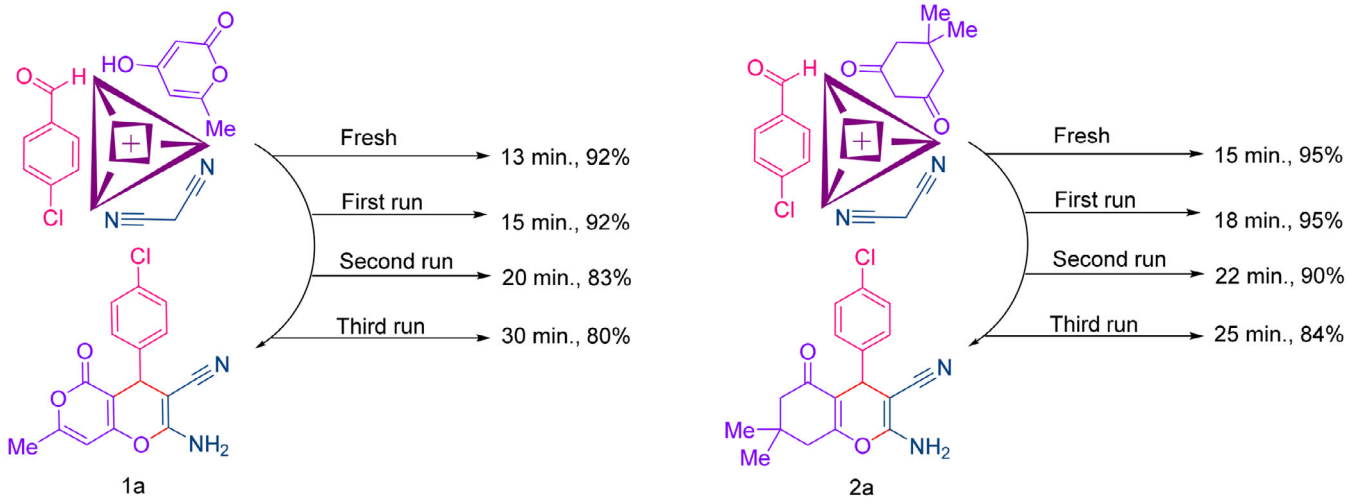
3.4.2 | Selected spectral data of the prepared structures

*2-Amino-7-methyl-5-oxo-4-(pyridin-3-yl)-4H,5H-pyrano [4,3-b]pyran-3-carbonitrile (**1e**)*

Melting point: 215–217°C. FT-IR (KBr, ν, cm^{-1}): 3,410, 3,127, 2,192, 1,704, 1,668, 1,647, 1,621, 1,379, 1,258. ^{1}H



SCHEME 7 A plausible mechanism for the synthesis of desired compound **2c**



SCHEME 8 Reusing test in both cases of multicomponent reactions

NMR (300 MHz, DMSO) δ_{ppm} 8.49–8.45 (m, 2H, Aromatic), 7.65–7.61 (m, 1H, Aromatic), 7.39–7.33 (m, 3H, Aromatic and NH_2), 6.31 (s, 1H, Olefinic), 4.40 (s, 1H, CH), 2.24 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 163.7, 161.8, 159.0, 158.7, 149.5, 148.7, 139.4, 135.7, 124.2, 119.6, 100.2, 98.5, 57.4, 34.5, 19.8.

*2-Amino-7-methyl-5-oxo-4-(3,4,5-trimethoxyphenyl)-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**1k**)*

Melting point: 227–229°C. FT-IR (KBr, ν, cm^{-1}): 3,498, 3,367, 2,195, 1,696, 1,669, 1,640, 1,589, 1,380, 1,130. ^{1}H NMR (300 MHz, DMSO) δ_{ppm} 7.21 (s, 2H, NH_2), 6.47 (s, 2H, Aromatic), 6.29 (s, 1H, Olefinic), 4.29 (s, 1H, CH),

3.75 (s, 6H, OCH_3), 3.66 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 163.3, 161.9, 158.7, 158.6, 153.3, 139.8, 137.0, 119.8, 105.2, 101.0, 98.5, 60.4, 58.3, 56.3, 36.9, 19.8.

*2-Amino-4-(3,5-difluorophenyl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**1l**)*

Melting point: 244–246°C. FT-IR (KBr, ν, cm^{-1}): 3,404, 3,330, 2,194, 1,708, 1,676, 1,645, 1,615, 1,382, 1,262. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.33 (s, 2H, NH_2), 7.12 (tt, 1H, Aromatic, J = 3 Hz), 7.01–6.94 (m, 2H, Aromatic), 6.30 (s, 1H, Olefinic), 4.43 (s, 1H, CH), 2.25 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 163.8, 162.8 (dd, J = 240 Hz, J = 12.8 Hz), 161.8, 159.2, 158.7, 148.7 (t, J = 8.25 Hz), 119.5, 111.3 (dd, J = 24 Hz, J = 7.25 Hz),103.0 (t, J = 25.5 Hz), 99.9, 98.6, 57.3, 36.5, 19.8.

*2-Amino-4-(3,5-bis[trifluoromethyl]phenyl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**1m**)*

Melting point: 248–250°C. FT-IR (KBr, ν, cm^{-1}): 3,421, 3,339, 2,194, 1,721, 1,675, 1,646, 1,611, 1,384, 1,284. ^1H NMR (300 MHz, DMSO) δ_{ppm} 8.02 (s, 1H, Aromatic), 7.96 (s, 2H, Aromatic), 7.41 (s, 2H, NH_2), 6.33 (s, 1H, Olefinic), 4.72 (s, 1H, CH), 2.25 (s, 1H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 164.0, 161.9, 159.3, 158.8, 147.3, 130.7 (q, J = 32.3), 129.2, 125.6, 122.0, 121.5, 119.4, 99.4, 98.7, 56.8, 36.4, 19.8.

*2-Amino-4-(4-isopropylphenyl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**1n**)*

Melting point: 222–225°C. FT-IR (KBr, ν, cm^{-1}): 3,370, 3,302, 2,203, 1,716, 1,671, 1,641, 1,617, 1,377, 1,264. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.21–7.19 (m, 3H, Aromatic and NH_2), 7.12 (d, 2H, Aromatic, J = 9 Hz), 6.29 (s, 1H, Olefinic), 4.26 (s, 1H, CH), 2.86 (s, 1H, CH, J = 6 Hz), 2.23 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.19 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 163.3, 161.9, 158.6, 158.6, 147.5, 141.5, 127.9, 126.8, 119.9, 101.4, 98.4, 58.5, 36.3, 33.5, 24.3, 24.3, 19.8.

*2-Amino-4-(4-isopropylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2h**)*

Melting point: 203–207°C. FT-IR (KBr, ν, cm^{-1}): 3,370, 3,311, 2,186, 1,682, 1,653, 1,370, 1,214, 1,137, 1,034. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.18 (d, 2H, aromatic, J = 9 Hz), 7.07 (d, 2H, Aromatic, J = 9 Hz), 6.99 (s, 2H, NH_2), 4.16 (s, 1H, CH), 2.86 (s, 1H, CH, J = 6 Hz), 2.53–2.52 (m, 2H, CH_2), 2.30–2.11 (AB system, 2H, CH_2, J = 15 Hz), 1.20 (d, 6H, CH_3, J = 6 Hz) 1.06 (s, 3H, CH_3), 0.99 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.2, 163.0, 158.9, 147.0, 142.7, 127.5, 126.8, 120.3, 113.3, 59.0, 50.5, 40.2, 35.6, 33.5, 32.3, 28.9, 27.4, 24.4, 24.3.

*2-Amino-4-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2o**)*

Melting point: 194–204°C. FT-IR (KBr, ν, cm^{-1}): 3,397, 3,331, 2,189, 1,687, 1,655, 1,607, 1,371, 1,141, 1,017. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.18 (td, 1H, Aromatic, J = 7.5 Hz), 7.03–6.96 (m, 2H, Aromatic), 6.90–6.85 (m, 3H, Aromatic and NH_2), 4.50 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 2.60–2.44 (AB system, 2H, J = 15 Hz), 2.30–2.06 (AB system, 2H, J = 15 Hz), 1.06 (s, 3H, CH_3), 0.99 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.0, 163.6, 159.5, 157.3, 132.7, 129.0, 128.3, 120.8, 120.3, 112.4, 112.0, 57.9, 56.1, 50.5, 32.3, 30.8, 29.1, 27.1.

*2-Amino-4-(3,5-difluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2p**)*

Melting point: 225–227°C. FT-IR (KBr, ν, cm^{-1}): 3,393, 3,327, 2,198, 1,682, 1,661, 1,602, 1,375, 1,307, 1,119. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.16 (s, 2H, NH_2), 7.08 (tt, 1H, Aromatic, J = 3 Hz), 6.92–6.85 (m, 2H, Aromatic), 4.30 (s, 1H, CH), 2.64–2.47 (AB system, 2H, CH_2, J = 18 Hz), 2.30–2.16 (AB system, 2H, CH_2, J = 18 Hz), 1.05 (s, 3H, CH_3), 1.00 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.2, 163.7, 162.8 (dd, J = 240 Hz, J = 12.8 Hz), 159.1, 150.0 (t, J = 8.3 Hz), 119.8, 112.02, 110.8 (dd, J = 24.7, J = 7.5 Hz), 102.7 (t, J = 25.5 Hz), 57.6, 50.7, 40.1, 35.8, 32.3, 28.5, 27.6.

*2-Amino-7,7-dimethyl-5-oxo-4-(4-[trifluoromethyl]phenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2q**)*

Melting point: 217–219°C. FT-IR (KBr, ν, cm^{-1}): 3,394, 3,323, 2,190, 1,683, 1,658, 1,371, 1,324, 1,119, 1,067. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.69 (d, 2H, aromatic, J = 6 Hz), 7.41 (d, 2H, aromatic, J = 6 Hz), 7.16 (s, 2H, NH_2), 4.33 (s, 1H, CH), 2.62–2.52 (m, 2H, CH_2), 2.31–2.11 (AB system, 2H, CH_2, J = 15 Hz), 1.06 (s, 3H, CH_3), 0.98 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.2, 163.4, 159.0, 128.6, 128.0, 127.5, 126.6, 125.8 (q, J = 3.75 Hz), 123.0, 120.0, 112.5, 57.9, 50.4, 40.2, 36.1, 32.3, 28.8, 27.4.

*2-Amino-4-(3,5-bis[trifluoromethyl]phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2r**)*

Melting point: 232–236°C. FT-IR (KBr, ν, cm^{-1}): 3,405, 3,334, 2,200, 1,683, 1,659, 1,374, 1,281, 1,131, 1,038. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.99 (s, 1H, Aromatic), 7.85 (s, 2H, Aromatic), 7.25 (s, 2H, NH_2), 4.57 (s, 1H, CH), 2.58 (brs 2H, CH_2), 2.32–2.10 (AB system, 2H, CH_2, J = 15 Hz), 1.06 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.33, 164.1, 159.4, 148.7, 130.7 (q, J = 32.3 Hz), 129.2, 128.5, 125.6, 121.0, 122.10, 119.7, 111.7, 57.3, 50.3, 40.1, 35.8, 32.3, 28.9, 26.9.

*2-Amino-4-(3,4-difluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2s**)*
Melting point: 184–188°C. FT-IR (KBr, ν, cm^{-1}): 3,394, 3,324, 2,188, 1,674, 1,638, 1,516, 1,365, 1,246, 1,214. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.42–7.33 (m, 1H, Aromatic), 7.24–7.17 (m, 1H, Aromatic), 7.12 (s, 2H, NH_2), 7.05–7.01 (m, 1H, Aromatic), 4.26 (s, 1H, CH), 2.60–2.47 (AB system, 2H, CH_2, $J = 18$ Hz), 2.29–2.13 (AB system, 2H, CH_2, $J = 15$ Hz), 1.05 (s, 3H, CH_3), 0.98 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.2, 163.3, 159.0, 149.6 (dd, $J = 247.5$, $J = 12.8$), 148.6 (dd, $J = 247.5$, $J = 12.8$) 143.1 (t, $J = 3.8$ Hz), 124.3–124.4 (m), 120.0, 117.2 (dd, $J = 90$ Hz, $J = 17.3$), 112.5, 58.0, 50.4, 40.1, 35.4, 32.3, 28.6, 27.5.

*2-Amino-4-(3,5-difluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2t**)*
Melting point: 239–241°C. FT-IR (KBr, ν, cm^{-1}): 3,406, 3,332, 2,192, 1,683, 1,657, 1,463, 1,367, 1,122, 1,004. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.15 (s, 2H, NH_2), 7.07 (tt, 1H, Aromatic, $J = 3$ Hz), 6.94–6.88 (m, 2H, Aromatic), 4.29 (s, 1H, CH), 2.74–2.60 (m, 2H, CH_2), 2.34–2.30 (m, 2H, CH_2), 2.01–1.92 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.4, 165.8, 162.8 (dd, $J = 240$ Hz, $J = 12.8$ Hz) 159.0, 150.0 (t, $J = 8.3$ Hz), 119.9, 113.0, 110.8 (dd, $J = 24$ Hz, $J = 9.8$ Hz),102.6 (t, $J = 25.5$), 57.5, 36.7, 35.8, 27.0, 20.2.

*2-Amino-5-oxo-4-(4-[trifluoromethyl]phenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2u**)*
Melting point: 209–212°C. FT-IR (KBr, ν, cm^{-1}): 3,430, 3,335, 2,197, 1,683, 1,658, 1,597, 1,422, 1,367, 1,105. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.68 (d, 2H, Aromatic, $J = 9$ Hz), 7.42 (d, 2H, Aromatic, $J = 9$ Hz), 7.14 (s, 2H, NH_2), 4.33 (s, 1H, CH), 2.73–2.57 (m, 2H, CH_2), 2.40–2.22 (m, 2H, CH_2), 2.04–1.87 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.4, 165.4, 159.0, 149.9, 130.2, 128.6, 127.7 (q, $J = 31.5$ Hz), 126.6, 125.8 (q, $J = 3.8$ Hz), 123.0, 120.0, 119.4, 113.5, 57.9, 57.8, 36.7, 36.1, 27.0, 20.2.

*2-Amino-4-(3,5-bis[trifluoromethyl]phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**2v**)*
Melting point: 256–259°C. FT-IR (KBr, ν, cm^{-1}): 3,407, 3,335, 2,195, 1,682, 1,657, 1,372, 1,282, 1,171, 1,124. ^1H NMR (300 MHz, DMSO) δ_{ppm} 7.98 (s, 1H, Aromatic), 7.87 (s, 2H, Aromatic), 7.24 (s, 2H, NH_2), 4.56 (s, 1H, CH), 2.75–2.58 (m, 2H, CH_2), 2.39–2.24 (m, 2H, CH_2), 2.02–1.89 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO) δ_{ppm} 196.6, 166.0, 159.0, 148.7, 130.7 (q, $J = 33.0$ Hz), 129.2, 128.6 (q, $J = 2.3$ Hz), 125.6, 122.0, 121.1, 119.7, 118.4, 112.6, 57.1, 36.7, 35.9, 27.1, 20.2.

4 | CONCLUSIONS

In summary, a novel hydrophilic bifunctional oxyammonium-based ionic liquid, namely, 2,2′-(ethane-1,2-diylbis[oxy])bis(ethan-1-aminium)-2,2,2-trifluoroacetate was designed, synthesized, and characterized using various techniques. The titled ionic liquid presents robust catalytic performance in the synthesis of pyrano[4,3-*b*]pyran derivatives and tetrahydrobenzo[*b*]pyrans. In addition, the ionic liquid presents a high potential of recycling and reusing capability in both types of the investigated reactions. The present work can open up new and promising insights into the course of rational design, synthesis, and applications of task-specific multifunctional hydrophilic ionic liquids for various purposes.

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