Journal of Molecular Liquids 259 (2018) 260–273

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Two novel binuclear sulfonic-functionalized ionic liquids: Influence of anion and carbon-spacer on catalytic efficiency for one-pot synthesis of bis(indolyl)methanes

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ARTICLE INFO

Article history:
Received 3 January 2018
Received in revised form 21 February 2018
Accepted 11 March 2018
Available online 13 March 2018

Keywords:
Binuclear sulfonic-functionalized ionic liquid
Carbon-spacer effect
Anion effect
Dual solvent-catalyst properties
Bis(indolyl)methane

ABSTRACT

Two new binuclear sulfonic-functionalized ionic liquids with four-carbon spacer were synthesized and their structures were characterized by FTIR, MS, ^{1}H and ^{13}C NMR; then some physical properties and pH of the aqueous solution of new task-specific ionic liquids were determined. Their dual solvent-catalytic activity were studied for the synthesis of bis(indolyl)methanes under mild conditions. The catalytic activity of these ionic liquids were compared with some ionic liquids derived from pyrazinium, piperazinium, benzimidazolium, imidazolium mono- or di-cation containing chloride and hydrogen sulfate as counter anion under optimized conditions. It was proved that the new ionic liquids containing two sulfonic imidazole moieties with four-carbon spacer as well as hydrogen sulfate as acidic counter anion were superior to the previously reported ionic liquids.

1. Introduction

Ionic liquids become alternative solvents, catalysts and extracting agents due to environmental perspectives including low vapor pressure, thermal and chemical stability, high ionic conductivity, tunable polarity and designable properties, immiscibility with some organic solvents simplified separation of products and potential reusability [1–5]. The majority of ionic liquids reported for organic transformations and catalysts have focused on imidazole or pyridine–based derivatives. Brønsted acidic ionic liquids (BAILs) containing SO_3H-functionalized on imidazole ring and an acidic counter anion as well as protonated imidazolium cation have been known to show dual solvent-catalyst properties with satisfactory conversion rates and selectivity for multicomponent reactions [6–9]. Nowadays, ionic liquids are used as an unconventional media for sustainable organic synthesis that allows selective separation of the desired products and catalysts in different phases, thus evading tedious and overpriced procedures which consume high volumes of toxic and volatile organic solvents. In this perspective, designing organic reactions in ionic liquid media is another attractive area in green chemistry [10,11].

The ionic liquid can be often recovered and reused. Often, the ionic liquid can be removed by water from the organic products using a simple workup. When a precious metal catalyst is used in the reaction, this procedure cannot be performed. In the other approach, the organic products can be extracted by nonpolar organic solvents and the remained ionic liquid can be concentrated and then directly recharged with new reactants for another run.

Bis(indolyl)methanes (**BIMs**) as a derivative of the substituted indoles have been achieved growing attention because of their broad spectrum of biological and pharmaceutical activities and their utility for drug design [12–14]. BIMs have been utilized as the colorimetric chemosensor for aspartate and glutamate in water as well as a simple tris-(indolyl)methane reported to detect fluoride anions by naked eye [15,16]. Therefore, a variety of synthetic protocols have been reported for the preparation of **BIMs**, and the electrophilic substitution reaction of indoles with carbonyl compounds in the presence Brønsted or Lewis acids is one of the most simple and important protocols. Lewis acids are often moisture sensitive as well as they will be deactivated by nitrogen atom present in indole and bis(indolyl)methane [17].

In pursuit of our studies on the preparation of new sulfonic-functionalized acidic ionic liquids and their applications as solvent or catalyst in a variety of the organic transformations [18–24], herein, two new binuclear sulfonic-functionalized ionic liquid (TSIL) with chloride and hydrogen sulfate counter anion were synthesized and their structures were characterized by FTIR, MS, ^{1}H and ^{13}C NMR. The physical properties of new TSILs were determined and their dual solvent–catalytic activity was investigated for the synthesis of the symmetric **BIMs** under mild conditions. Also, the effect of the presence of the four-carbon spacer and acidic anion on the catalytic activity of these TSILs were studied in comparison with some previously reported sulfonic-functionalized ILs.

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https://doi.org/10.1016/j.molliq.2018.03.044
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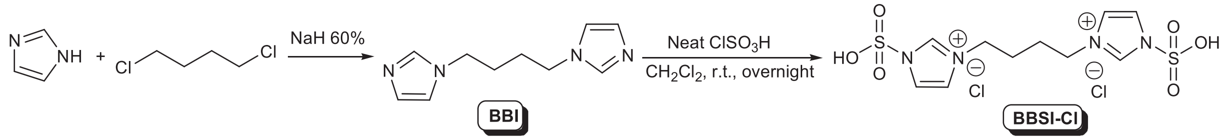
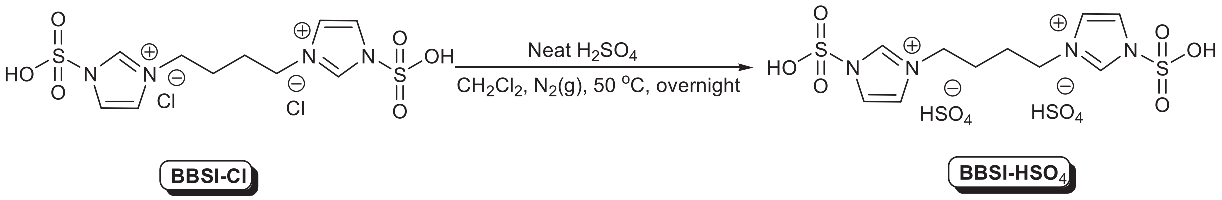


Scheme 1. Synthesis of 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride **BBSI-Cl**.



Scheme 2. Synthesis of 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) hydrogen sulfate **BBSI-HSO$_4$**.

2. Results and discussion

*2.1. Synthesis of 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride **BBSI-Cl** and 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) hydrogen sulfate **BBSI-HSO$_4$** and the characterization of their structures*

1,1′-Butylenebis(3-sulfo-3H-imidazol-1-ium) chloride (**BBSI-Cl**) was prepared in two steps (Scheme 1). At the first step, two equivalents of imidazole were alkylated by one equivalent 1,4-dichlorobutane in DMSO in the presence of two equivalent NaH as a base reagent at room temperature. The resulting white solid 1,1′-(1,4-butanediyl)bis(imidazole) (**BBI**) then was transformed into **BBSI-Cl** using two equivalent neat chlorosulfonic acid as the sulfonating reagent in CH_2Cl_2 at room temperature overnight. The resulting ionic liquid was isolated as viscous colorless liquid and the structure of **BBSI-Cl** was characterized by FTIR, MS, ^1H and ^{13}C NMR.

Then, neat sulfuric acid was added dropwise to **BBSI-Cl** in CH_2Cl_2 over a period of 2 min at room temperature. The resulting mixture was stirred for overnight at 50 °C under a continuous flow of nitrogen to remove the hydrogen chloride gas released during the reaction (Scheme 2). The

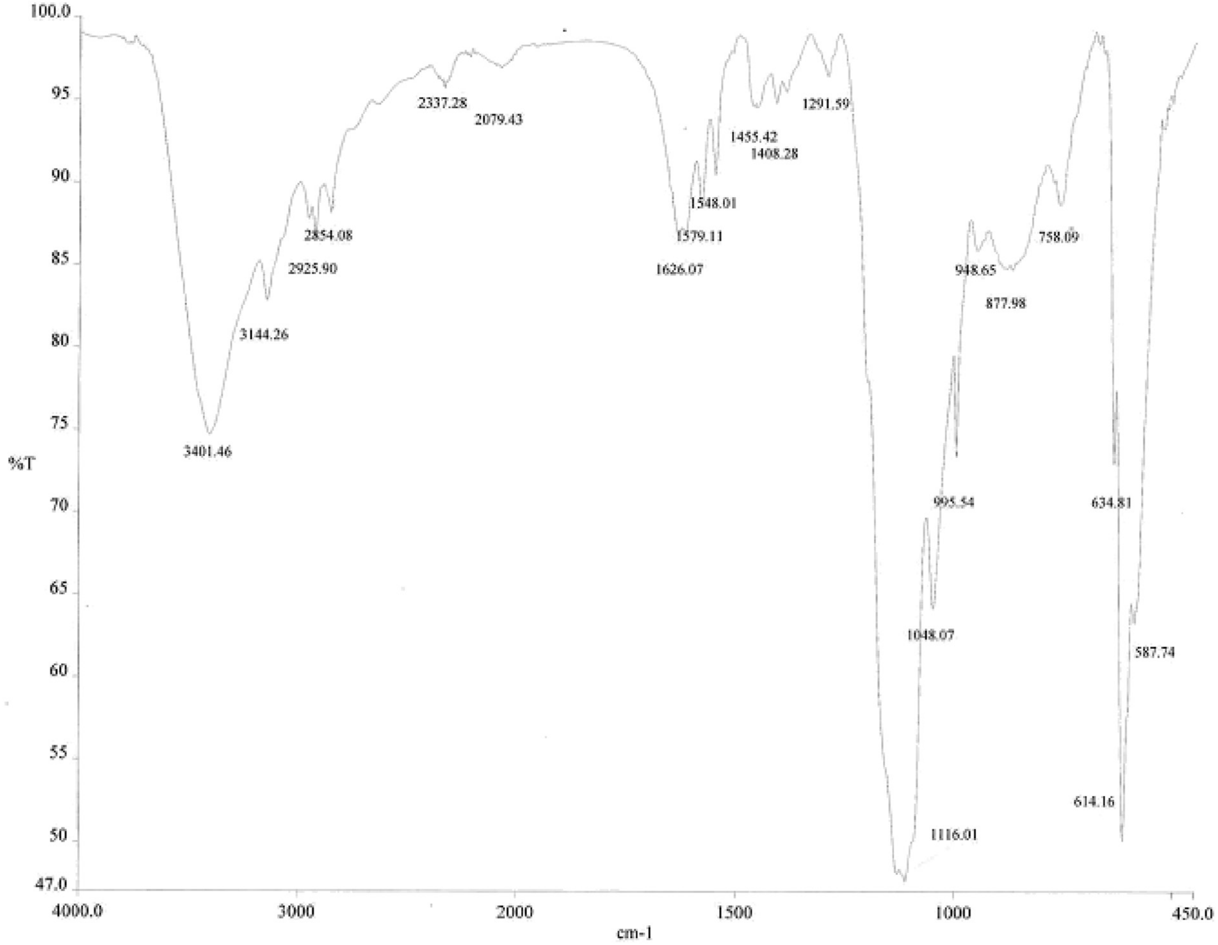


Fig. 1. FTIR Spectra of 1,1′-butylenebis(3-sulfo-3*H*-imidazol-1-ium) chloride **BBSI-Cl**.

resulting **BBSI-HSO$_4$** was isolated as a viscous yellow liquid which its structure was confirmed by FTIR, MS, ^{1}H and ^{13}C NMR.

FTIR spectra of 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride **BBSI-Cl** and 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) hydrogen sulfate **BBSI-HSO$_4$** are presented in Figs. 1 and 2. The broad absorption at range 3500–3200 cm^{-1} is assigned to O—H stretching vibration of the hydroxyl groups in sulfonic and hydrogen sulfate moieties as well as the moisture absorbed by the sample. The C—H stretching vibrations of **BBSI-Cl** and **BBSI-HSO$_4$** were observed at 3144, 3152, 2925, 2878 and 2854 cm^{-1} which are the characteristic region for the ready identification of C—H stretching vibrations [25,26]. The bands between 1680 and 1540 cm^{-1} are due to C=C and C=N stretching vibrations [27]. The identification of C—N stretching frequency is a very difficult task since the mixing of bands is possible in this region; hence, the FTIR bands at 1455, 1454 and 1408 cm^{-1} have been designated to C—N stretching modes of vibrations [28]. A series broad and strong peaks due to the SO$_2$ asymmetric and symmetric vibrations were observed at range 1200–1000 cm^{-1} [29–31]. The sharp peaks at 1048 and 1017 cm^{-1} can be assigned to S—OH bend of hydrogen sulfate anion and sulfonic groups according to the bending vibration in sulfuric acid and a variety of the sulfonic acid-functionalized compounds [32]. **BBSI-Cl** and **BBSI-HSO$_4$** exhibit N—S stretching vibrational absorption in the region 950–860 cm^{-1} as a series of the medium intensity bands [33]. The bands at 635, 620, 614, 588 and 568 cm^{-1} have been designated to ring deformation out-of-plane-bending. The C—H out-of-plane-bending peaks and C—H in plane-bending can be observed at 996, 949, 758 and 751 cm^{-1} [27].

^{1}H NMR Spectra of **BBSI-Cl** and **BBSI-HSO$_4$** in DMSO-d$_6$ gave sharp signals (Figs. 3 and 4). Acidic hydrogen of sulfonic groups in **BBSI-Cl** gave a broadened singlet centered at 3.66 ppm, whose shift displacement indicates that the acidic hydrogens were involved in strong hydrogen bonds in DMSO d$_6$ while for **BBSI-HSO$_4$**, acidic hydrogen of hydrogen sulfate anions was observed as a broad peak at 14.32 ppm, thus they were not involved in hydrogen-bonding as well as it seems that acidic hydrogens sulfonic groups were less involving in H-bonding and a downfield shift to 6.65 ppm was exhibited in comparison to **BBSI-Cl**. Three aromatic protons attached to imidazole ring gave a set of three well-resolved signals at 9.16 as one singlet, as well as at 7.79 ppm and 7.69 ppm as two pseudotriplet (doublet-doublet) (dd) with a same coupling constant 1.5 Hz for **BBSI-Cl**. The three aromatic protons of **BBSI-HSO$_4$** were observed at 9.11 ppm as one singlet, 7.77 ppm as one doublet-doublet (dd) with coupling constant 1.6 and 1.5 Hz, and 7.66 ppm as one doublet-doublet (*dd*) with coupling constant 1.6 and 1.4 Hz.

Aliphatic protons for **BBSI-Cl** were displayed as two well-resolved signals at 4.26 ppm and 1.85–1.76 ppm, respectively. The signal at 4.26 ppm can be assigned to the protons of alkyl group N–C$\underline{\mathbf{H_2}}$ since their multiplicities correspond to a triplet (t) with coupling constant ^{3}J = 5.9 Hz and the signal at 1.81–1.78 ppm as a multiplet (m) can be appointed to the protons alkyl N—CH$_2$—C$\underline{\mathbf{H_2}}$. Aliphatic protons for **BBSI-Cl** were also observed at 4.26 ppm as one triplet (t) with coupling constant 5.7 Hz for alkyl group N—C$\underline{\mathbf{H_2}}$ and one multiplet (m) at 1.80–1.77 ppm for the alkyl N—CH$_2$—C$\underline{\mathbf{H_2}}$, respectively.

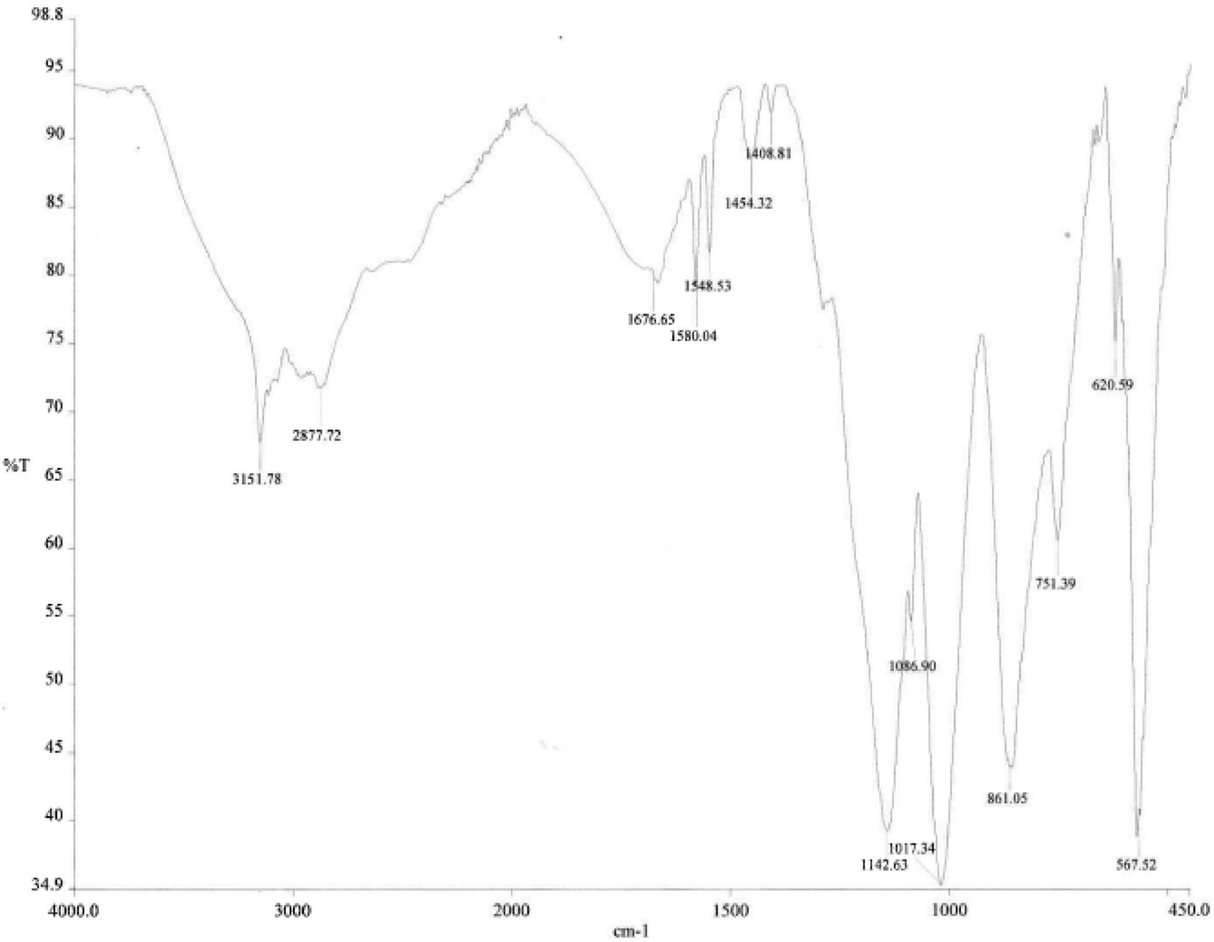


Fig. 2. FTIR Spectra of 1,1′-butylenebis(3-sulfo-3*H*-imidazol-1-ium) hydrogen sulfate **BBSI-HSO$_4$**.

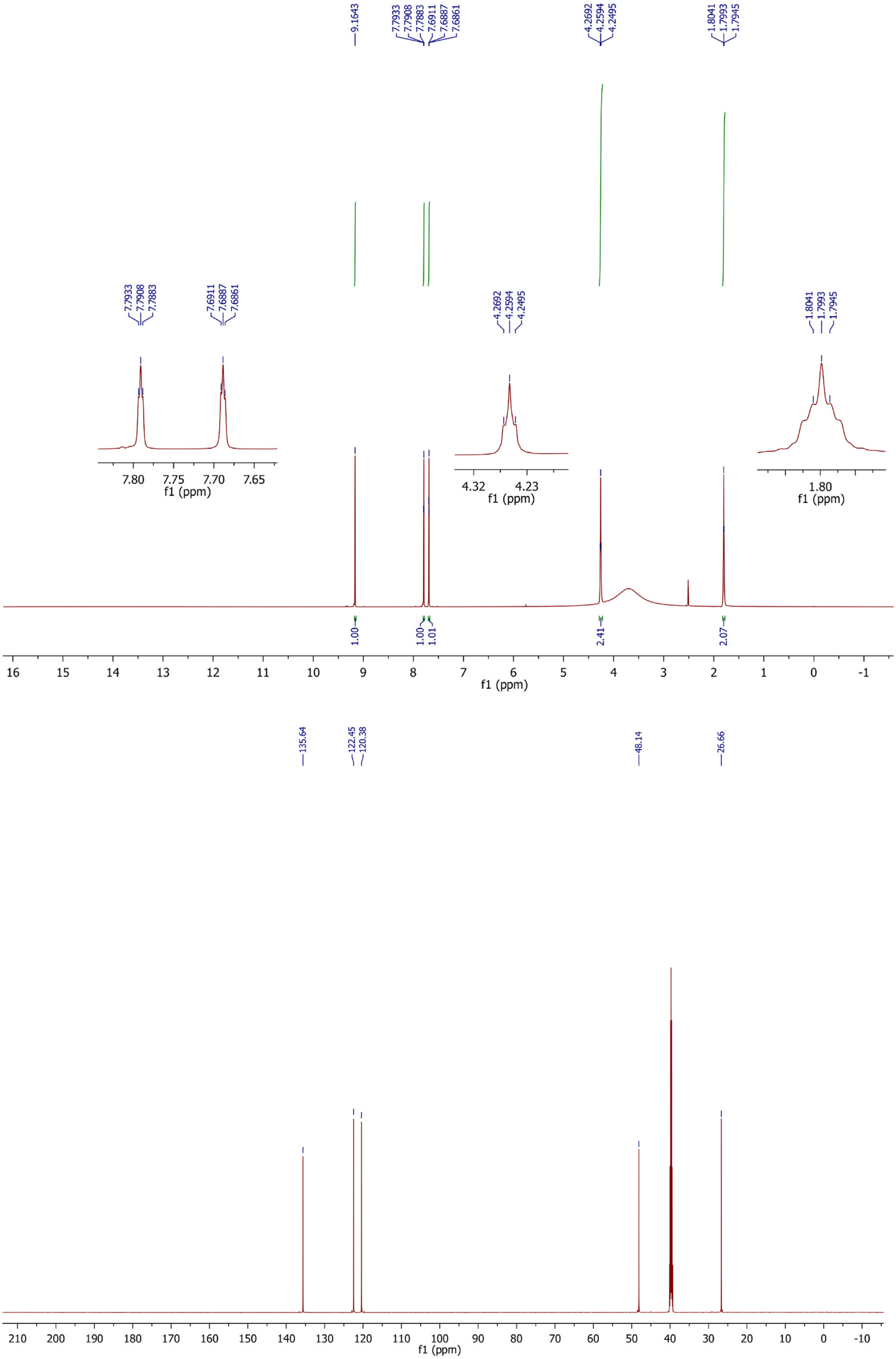
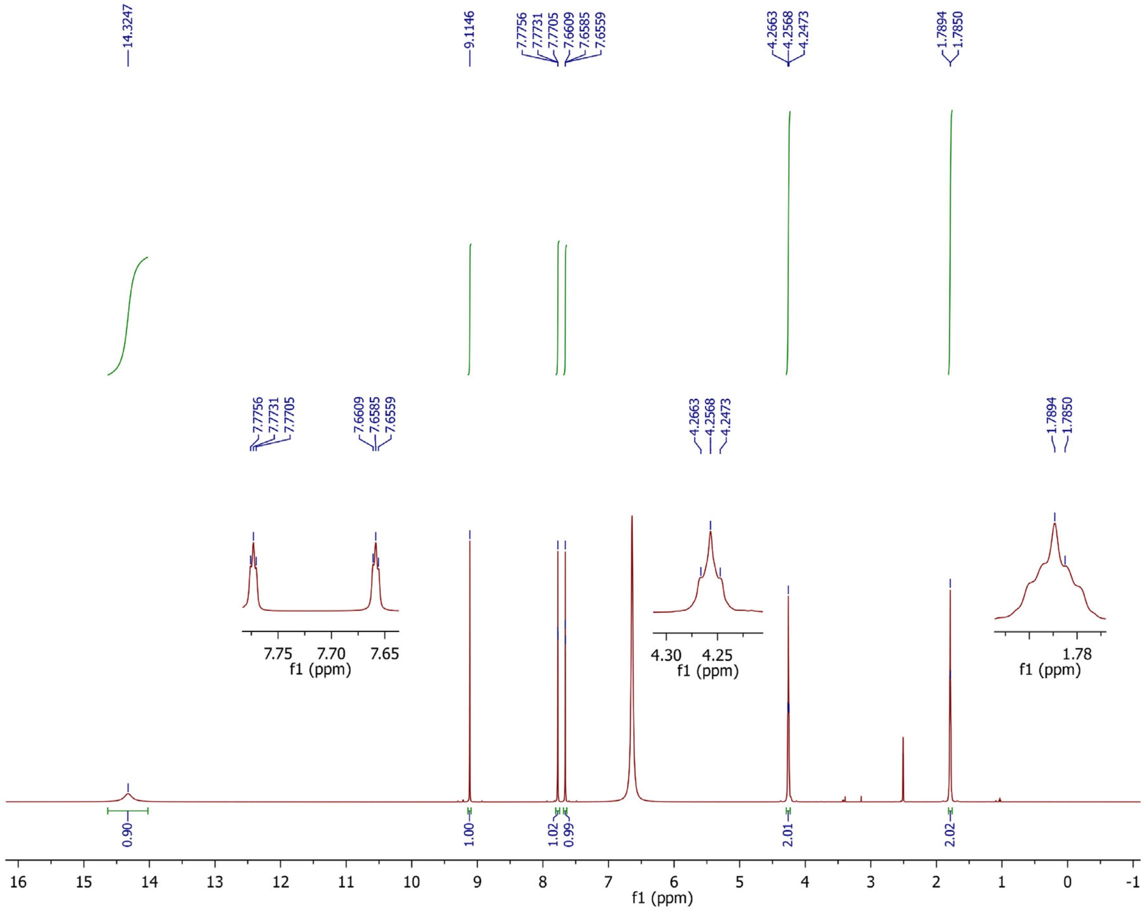


Fig. 3. ^{1}H and ^{13}C NMR Spectra of 1,1′-butylenebis(3-sulfo-3*H*-imidazol-1-ium) chloride (**BBSI-Cl**).



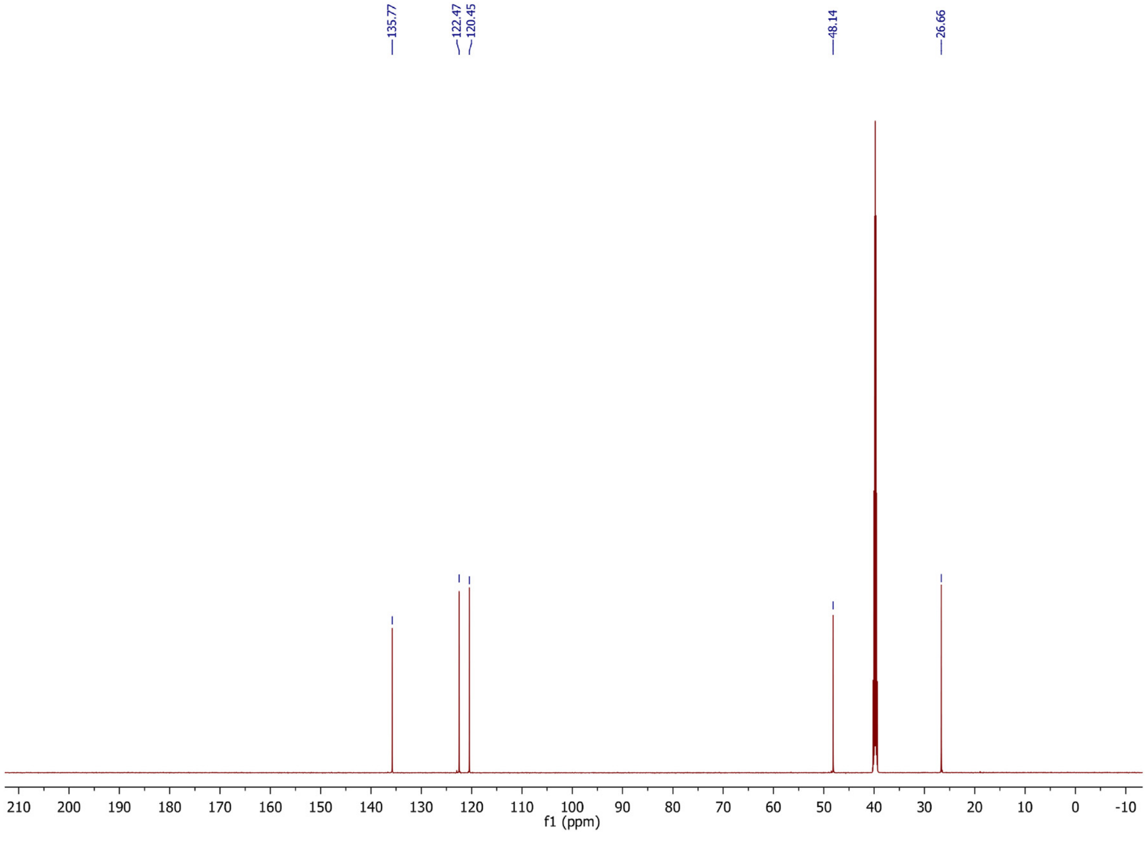


Fig. 4. ^{1}H and ^{13}C NMR Spectra of 1,1′-butylenebis(3-sulfo-3*H*-imidazol-1-ium) hydrogen sulfate (**BBSI-HSO$_4$**).

^{13}C NMR experiment displays one signal for each of five carbon atoms in the structure of **BBSI-Cl** with chemical shifts 135.6, 122.4 and 120.4 ppm for imidazole ring, 48.1 ppm for N-$\underline{C}H_2$ and 26.7 ppm for N-CH$_2$-$\underline{C}H_2$ for carbon atoms in butane chain, respectively. ^{13}C NMR of **BBSI-HSO$_4$** also showed five signal at 135.8, 122.5 and 120.4 ppm for imidazole ring carbons and 48.1 and 26.7 ppm for N-$\underline{C}H_2$ and N-CH$_2$-$\underline{C}H_2$, respectively.

The cations of $C_{10}H_{15}N_4^+$ and $C_{10}H_{14}N_4Na^+$ were detected at m/z 191.1 [**BBI** + H]$^+$ and 213.1 [**BBI** + Na]$^+$ by positive ion mode LC-ESI-MS for 1,1′-(1,4-butanediyl)bis(imidazole) and the cations $C_{10}H_{15}N_4O_6S_2^+$ and $C_{10}H_{17}N_4O_6S_2^+$ were observed at m/z 351.2 [**BBSI**]$^+$ and 353.2 [**BBSI** + H$^+$] for **BBSI-Cl** and **BBSI-HSO$_4$** by positive ion mode LC-ESI-MS (Figs. 5 and 6).

The density of **BBSI-Cl** and **BBSI-HSO$_4$** were 1.21 and 1.45 g/mL at 27.00 ± 0.02 °C, respectively; which were measured by using a Mettler Toledo DM45 Deltarange Density meter and its calibration was performed using doubly distilled and degassed water and dried air at atmospheric pressure. The viscosity of **BBSI-Cl** and **BBSI-HSO$_4$** were 632 ± 2 and 811 ± 2 cP at 27.00 ± 0.02 °C, respectively which were performed with a Brookfield DV-III Ultra Viscometer.

The hydrophilic ILs readily absorb moisture from the atmosphere during storage; therefore, the exactly amount of water in **BBSI-Cl** and **BBSI-HSO$_4$** were determined by Karl Fisher (KF) titration, using a Metrohm 831 KF coulometer in conditions of ambient humidity and room temperature. The conditions of temperature, pressure and drying time were 100 °C, 80 mbar, and 12 h, respectively. The water content in **BBSI-Cl** and **BBSI-HSO$_4$** were 0.28 ± 0.02 wt% and 0.42 ± 0.02 wt%, respectively. The 0.01 M solutions of **BBSI-Cl** and **BBSI-HSO$_4$** were prepared in the deionized water and the pH readings were recorded with a pH meter F-71, LAQUA-HORIBA Scientific at 27 ± 1 °C. The pH of 0.01 M aqueous solution of **BBSI-Cl** and **BBSI-HSO$_4$** were 2.9 ± 0.1 and 2.2 ± 0.1, respectively. The standard deviation was obtained from three replicate determinations on the different three days. The new ionic liquid **BBSI-Cl** and **BBSI-HSO$_4$** were immiscible with ethyl acetate, n-hexane, and toluene but readily soluble in water, methanol, ethanol, acetic acid.

*2.2. Synthesis of bis(indolyl)methanes in the presence of **BBSI-Cl** and **BBSI-HSO$_4$***

Initially, the reaction of 4-chlorobenzaldehyde and indole as the model reaction was studied in the absence of catalyst and solvent at room temperature. The model reactants were ground using the planetary ball mill to afford the desired product in trace yield with 4 h reaction time at room temperature, confirming demand catalyst for this reaction. Next, the model reactants were taken up in **BBSI-Cl** as a dual solvent-catalyst reagent and the mixture was stirred for a reaction time 30 min at room temperature. The crude product was extracted with EtOAc, then the extracted organic phases were dried over Na$_2$SO$_4$ and the solvent was removed under vacuum rotary vaporization and the product directly purified by flash chromatography to afford the desired product (**3d**) in 54% yield (Table 1, entry 2). When the amount of ionic liquid was doubled, yield was improved to 84% (Table 1, entry 3) but further increasing the loading of ionic liquid led to a drop in yield to 79% (Table 1, entry 4). Decreasing the reaction time at the optimized loading ionic liquid results in a decrease in yield to 74% (Table 1, entry 5) whereas increasing reaction time to 45 min improved yield slightly (Table 1, entry 6). The yield was improved to 91% when the model reaction was performed at 50 °C under optimized conditions (Table 1, entry 7). At optimal temperature, decreasing the reaction time to 20 min cause to reduce of yield very slightly but further reduction of the reaction time lowered the yield of the desired product significantly (Table 1, entries 8 and 9).

Then we performed the model reaction in the presence of **BBSI-HSO$_4$** under aforementioned optimal conditions which afforded **3d** in 96% yield (Table 2, entry 1). The same yield was observed when the model reaction was done at room temperature for 20 min and **3d** was obtained in 91% yield when the model reaction was carried out at room temperature for 10 min (Table 2, entries 2 and 3). Further decreasing the reaction time to 5 min led to reducing of yield (Table 2, entry 4). The stirring of the reaction mixture became hard when we tried to perform the model reaction in the presence of 1 mL of **BBSI-HSO$_4$** per 2 mmol of 4-chlorobenzaldehyde and **3d** was isolated in 64% yield since mass transfer into viscous medium will be generally slower

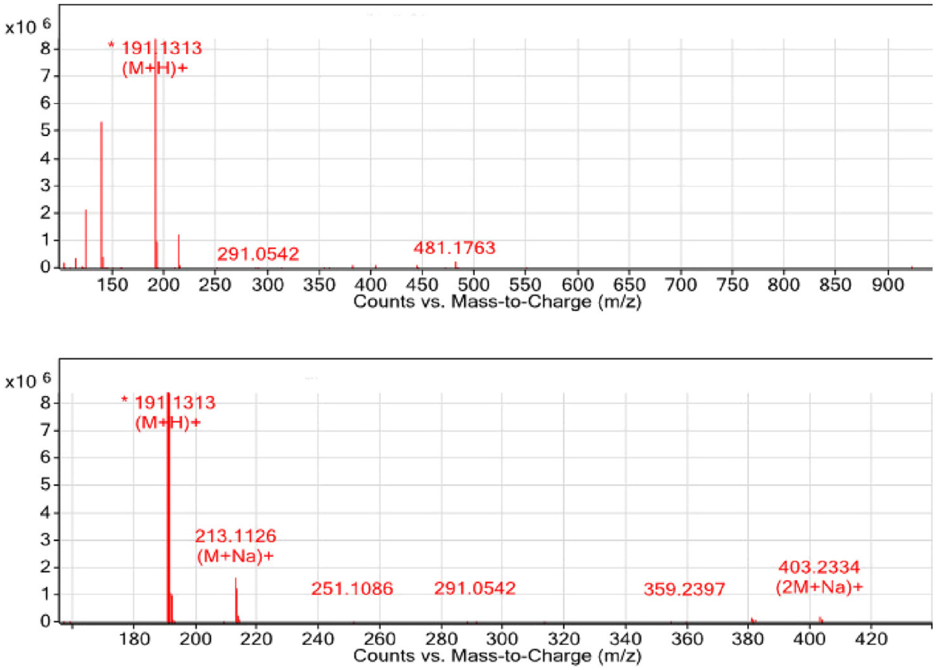


Fig. 5. Detection of [**BBI** + H]$^+$ ($C_{10}H_{15}N_4^+$) and [**BBI** + Na]$^+$ ($C_{10}H_{14}N_4Na^+$) ions by positive ion mode LC-ESI-MS.

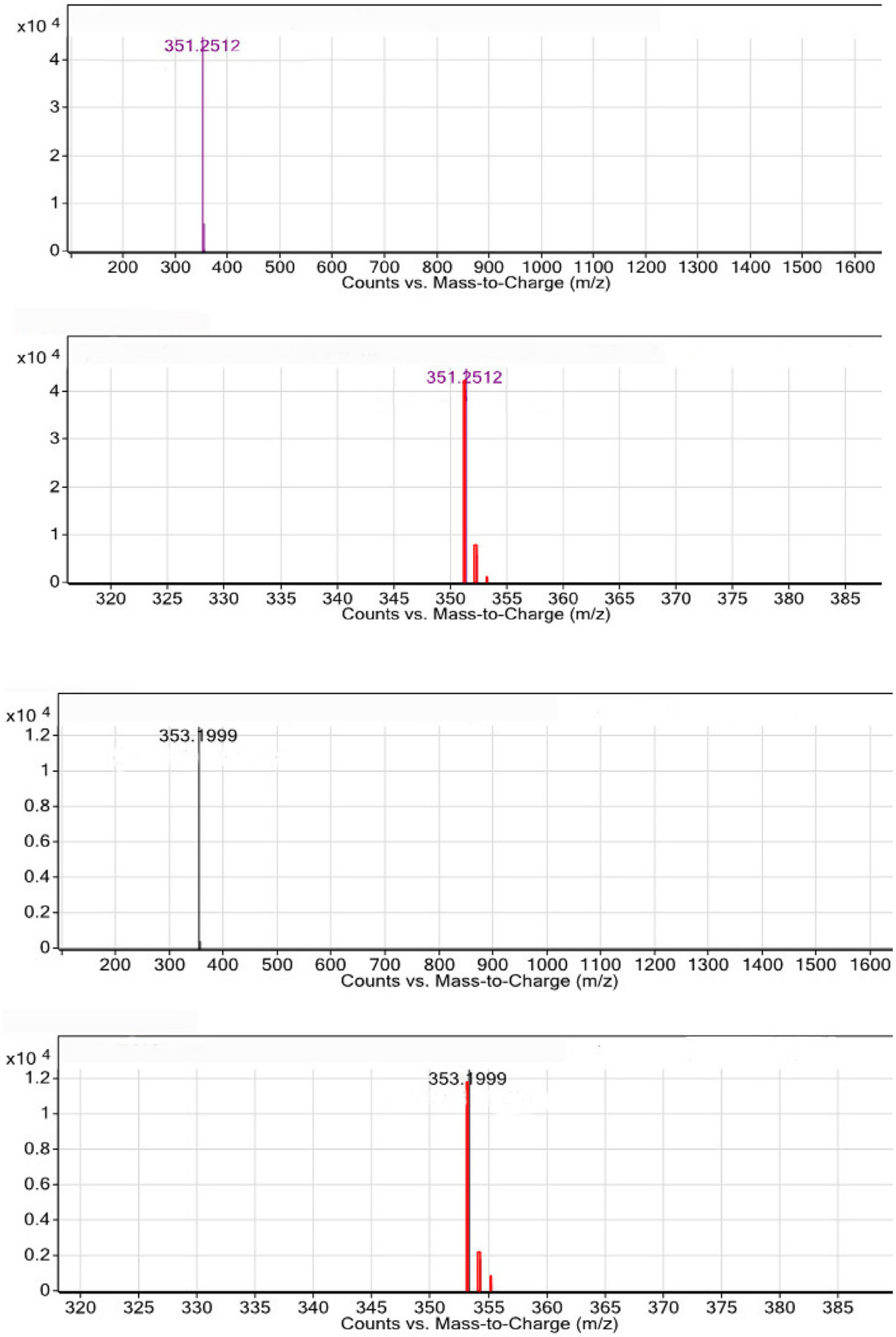


Fig. 6. Detection of [**BBSI**]$^+$ ($C_{10}H_{15}N_4O_6S_2^+$) and **BBSI** + H$^+$ ($C_{10}H_{17}N_4O_6S_2^+$) ions in **BBSI-Cl** and **BBSI-HSO$_4$** by positive ion mode LC-ESI-MS.

(Table 2, entry 5). Thus we performed the model reaction in 1.5 mL of IL which gave **3d** in 90% yield (Table 2, entry 6). **3d** was produced in 96% yield by increasing the reaction time to 20 min but there was no enhancement in yield when the reaction time was extended to 45 min (Table 2, entries 7 and 8).

The scope of the synthesis of **BIMs** via this protocol was evaluated by utilizing a variety of aldehydes **1**(**a**–**h**) and two indole derivatives viz., indole and 5-bromo-1*H*-indole under optimized conditions based on entries 8 and 7 in Tables 1 and 2, respectively (Scheme 3).

BIMs containing a broad range of substituents were prepared in good yield, as shown in Table 3. When 5-bromo-1*H*-indole, instead of indole, was utilized in the optimized reaction conditions, the desired BIMs were afforded in slightly lower yields (Table 3, entries 11–19). The aldehydes bearing electron-withdrawing or donating substituents in the aromatic ring gave the desired BIMs in good to excellent yields. Aldehydes bearing electron-withdrawing substituents afforded a higher yield of BIMs than electron-donating substituents at same position and conditions. With electron-withdrawing substituents such as nitro (—NO$_2$) in the *para*-position of aryl aldehydes, the electrophilicity of

Table 1
Optimization of the synthesis of **BIMs** under a variety of reaction conditions.[a]

Entry	Loading **BBSI-Cl** as dual solvent-catalyst (mL)	Temperature (°C)	Reaction time (min)	Yield (%)[b]
1	0	r.t.	240	Trace[c]
2	1	r.t.	30	54
3	2	r.t.	30	84
4	3	r.t.	30	79
5	2	r.t.	15	74
6	2	r.t.	45	85
7	2	50	30	92
8	**2**	**50**	**20**	**91**
9	2	50	10	76

[a] Reaction conditions: 4-chlorobenzaldehyde (**2d**) (2.0 mmol), indole (4.0 mmol).
[b] Isolated yield.
[c] Monitored by GC–MS.

Table 2
Optimization of the synthesis of **BIMs** under a variety of reaction conditions.[a]

Entry	Loading ***BBSI*-HSO$_4$** as dual solvent-catalyst (mL)	Temperature (°C)	Reaction time (min)	Yield (%)[b]
1	2	50	20	96
2	2	r.t.	20	96
3	2	r.t.	10	91
4	2	r.t.	5	68
5	1	r.t.	10	64
6	1.5	r.t.	10	90
7	**1.5**	**r.t.**	**20**	**96**
8	1.5	r.t.	45	96

[a] Reaction conditions: 4-chlorobenzaldehyde (**2d**) (2.0 mmol), indole (4.0 mmol).
[b] Isolated yield.

the carbonyl group is enhanced while electron-donating groups such as methoxy (—OCH$_3$) in the same position, clearly decrease the electrophilicity of carbonyl group. Aldehydes bearing substituents at *ortho*-position afforded a lower yield of **2** than same substituents at *para*-positions (Table 3, entries 4 and 5) due to the steric hindrance effect. As shown in Table 3, the acid sensitive aldehydes such as 4-methoxybenzaldehyde and Furan-2-carboxaldehyde afforded the desired product in good yield without any decomposition and isomerization under the optimized reaction conditions (Table 3, entries 3,8,13, and 16). Furthermore, heterocyclic aldehydes containing sulfur also gave the desired BIMs in moderate to good yield (Table 3, entries 9 and 17).

The catalytic efficiency of **BBSI-HSO$_4$** was higher than **BBSI-HSO$_4$** because the reaction was performed at low temperature and shorter reaction time in the presence of lower amount of IL which can be attributed to the presence of acidic anion. Nevertheless, no significant difference were observed in the yields of some desired products (Table 3, entries 6,10,11,17,19).

Interestingly, one equivalent of terephthalaldehyde reacted with four equivalents of indole and 5-bromo-1*H*-indole to give the desired di-bis(indolyl)methanes (**3j** and **3r**) in 74%, 76% and 65%, 72% yield for **BBSI-Cl** and **BBSI-HSO$_4$**, respectively (Table 3, entries 10 and 18) (Scheme 4).

In order to study of chemoselectivity, the reaction was performed between one equivalent of 4-acetylbenzaldehyde and two equivalents of indole under optimized conditions. As results shown, the high chemoselectivity of the present protocol was verified and 1-{4-[bis(5-bromo-1*H*-indol-3-yl)methyl]phenyl}ethanone (**3s**) was obtained in 82% and 84% yield in the presence of **BBSI-Cl** and **BBSI-HSO$_4$**, respectively. In another experiment, a mixture of benzaldehyde and acetophenone was allowed to react with two equivalents indole for 20 min under the optimized conditions. The result showed that only bis-(1*H*-indol-3-yl)methyl benzene (**3i**) was found in 78% and 84% yield as sole product in the presence of **BBSI-Cl** and **BBSI-HSO$_4$**, respectively; and acetophenone did not react at all with indole under the optimized reaction conditions (Scheme 5).

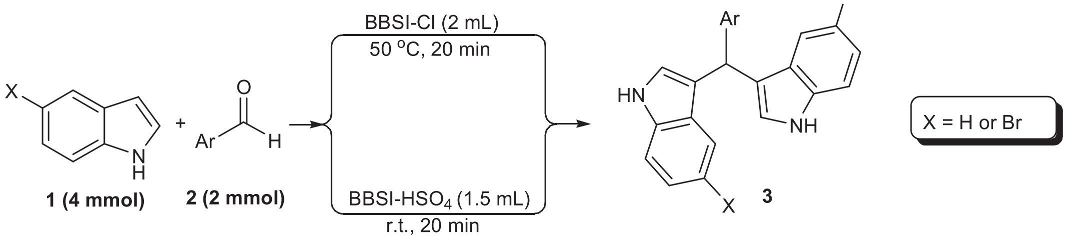
Although the mechanism for the current transformation has been reported in the literature [17,42], a plausible mechanism has been presented in Scheme 6. In the first step, **BBSI-Cl** and **BBSI-HSO$_4$** play dual activation role through the formation of intermediates involving hydrogen bond formation between the carbonyl group and the C-2 hydrogen atom and acidic hydrogen sulfonic groups of the IL cation as well as hydrogen sulfate anion, electrostatic interaction between the quarternary nitrogen atom of the **BBSI-Cl** cation with the nitrogen lone pair of electrons of the indole as well as the formation of hydrogen bond between the indole N—H hydrogen atom and chloride counter anion of **BBSI-Cl**. **BBSI-Cl** and **BBSI-HSO$_4$** may also serve as a dehydrating agents to facilitate the formation of azafulven (**I**) [43,44]. Then a second iodole molecule attack to azafulven (**I**) as an intermediate and the final product is afforded.

As one can see in Table 4, the present protocol show a very good comparability with the reported methods in literature when all terms such as yield, reaction time, workup, mild conditions, catalyst loading, reusability, and sustainability are taken into account.

Then, the catalytic activity of mono and di-cationic ionic liquids containing mono- and di-sulfonic group(s) along with chloride and hydrogen sulfate counter anion has been explored to catalyze the reaction of indole with 4-chlorobenzaldehydes to afford **3d** under aforementioned optimized conditions (Table 5). The sulfonic acid-functionalized pyrazinium, piperazinium, benzimidazolium, imidazolium ionic liquids were prepared according to the literature [51–54].

Sulfonic acid-functionalized piperizanium chloride [PiS-Cl], Sulfonic acid-functionalized pyrazinium chloride [PzS-Cl], Sulfonic acid-functionalized pyrazinium propyl chloride [PzPS-Cl], Sulfonic acid-functionalized imidazolium chloride [DSI-Cl], Sulfonic acid-functionalized imidazolium hydrogen sulfate [DSI-HSO$_4$].

As shown in Table 5, the solvent-catalytic efficiency of these ILs derived from pyrazinium, piperazinium, benzimidazolium, imidazolium cation containing chloride as counter anion is influenced by the structure of the cationic moiety following the order:



Scheme 3. Synthesis of BIMs in the presence of **BBSI-Cl** under optimal conditions.

Table 3
Telescopic Synthesis of BIMs in the presence of **BBSI-Cl** and **BBSI-HSO$_4$** under optimized reaction conditions.[a]

Entry	Indole derivatives (**1**)	Aldehydes **2**(**a**–**h**)	BIMs (**3**)	Yield (%)[b]		Melting point (°C)	
				BBSI-Cl	**BBSI-HSO$_4$**	Found	Reported (ref.)
1	Indole	C_6H_5-	a	91	95	125–127	128–130 [34]
2		4-CH_3-C_6H_4-	b	92	96	92–94	92–94 [35]
3		4-CH_3O-C_6H_4-	c	88	92	180–181	186–188 [35]
4		4-Cl-C_6H_4-	d	91	96	103–105	102.7–104.2 [36]
5		2-Cl-C_6H_4-	e	86	92	77–79	77–78 [42]
6		4-NO_2-C_6H_4-	f	96	96	217–219	220–222 [35]
7		3-NO_2-C_6H_4-	g	92	93	259–260	261–263 [42]
8		Furan-2-carboxaldehyde	h	84	92	>300	322–325 [37]
9		Thiophene-2-carboxaldehyde	i	82	86	182–184	186–188 [38]
10		Terephthaldehyde	j	74	76	245–247	246.5–248 [36]
11	5-Bromoindole	C_6H_5-	k	90	91	248–250	253.4–255 [36]
12		4-CH_3-C_6H_4-	l	84	87	210–212	–
13		4-CH_3O-C_6H_4-	m	82	87	246–248	–
14		4-Cl-C_6H_4-	n	86	90	145–147	145–147 [39]
15		4-NO_2-C_6H_4-	o	89	91	219–221	189–190 (dec.) [40]
16		Furan-2-carboxaldehyde	p	78	81	183–185	–
17		Thiophene-2-carboxaldehyde	q	75	75	178–180	177–179 [41]
18		Terephthaldehyde	r	65	72	210 (dec.)	210 (dec.) [39]
19		4-Acetylbenzaldehyde	s	82	84	115–117	–

[a] Reaction conditions: indole or 5-bromo-1H-indole (**1**) (4.0 mmol), aldehyde (**2a–q**) (2.0 mmol), **BBSI-Cl** (2.0 mL) at 50 °C or **BBSI-HSO$_4$** (1.5 mL) at room temperature, reaction time (20 min).
[b] Isolated yield.

BBSI-Cl > DSI-Cl > DSBI-Cl > PzPS-Cl > PzS-Cl > PiS-Cl. The best result was obtained with the BBSI-Cl and much reduction of the catalytic effect was observed with pyrazinium and piperazinium ILs. The catalytic property was retained with PiS-Cl although to a more extent with respect to PzS-Cl which its reason may be the presence of two sulfonic groups per IL molecules (Table 5, entry 1). Introduction of a three-carbon spacer linking sulfonic group to the pyrazinium cation at PzPS-Cl exhibited a marked increase in catalytic activity of IL with respect to its analogue with no spacer viz. PzS-Cl (Table 5, entries 2 and 3). It seems that the presence and number of the C-2 hydrogen per imidazole-based IL for DSI-Cl and BBSI-Cl increased the catalytic efficiency (Table 5, entries 4,6,7). Also the catalytic activity ILs containing hydrogen sulfate counter anion was more than that with chloride anion for same cation ionic liquid (Table 5, entries 5,6 and 7,8).

2.3. Reusability of **BBSI-Cl** and **BBSI-HSO$_4$**

The ionic liquid can be often recovered and reused. Often, the ionic liquid can be removed by water from the organic products using a simple workup. In some cases that this procedure cannot be performed, the organic products can be extracted by nonpolar organic solvents and the remained ionic liquid can be concentrated and then directly recharged with new reactants for another run. In the present protocol, after completion of the reaction, the desired BIMs were readily extracted using ethyl acetate or ether because new ionic liquids **BBSI-Cl** and **BBSI-HSO$_4$** are insoluble in these organic solvents and the remained ionic liquid was concentrated under reduced pressure and recharged with new model reactants for another run. **2d** was obtained in an average 90% and 95% yield for three subsequent runs in the presence of **BBSI-Cl** and **BBSI-HSO$_4$**, respectively. The catalytic activity of the recycled liquid acid showed almost no significant loss even after three consecutive runs. Furthermore, the structure of reused **BBSI-Cl** and **BBSI-HSO$_4$** were analyzed by ^{1}H NMR in DMSO d$_6$ after the third run. As observed in Fig. 7 and 8, the chemical structure of **BBSI-Cl** and **BBSI-HSO$_4$** showed no significant change under the present workup.

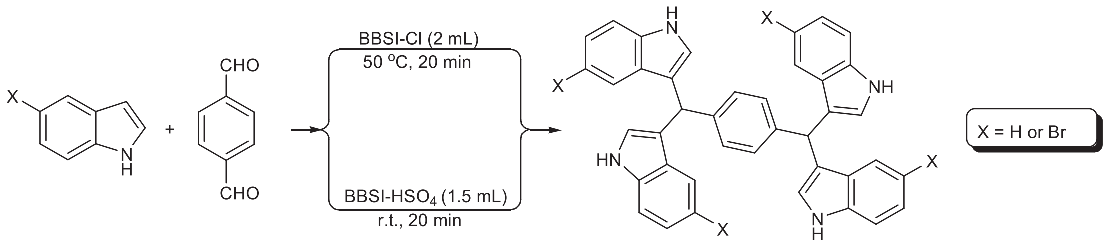
3. Experiment

3.1. Materials

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and FTIR, NMR and elemental analysis. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

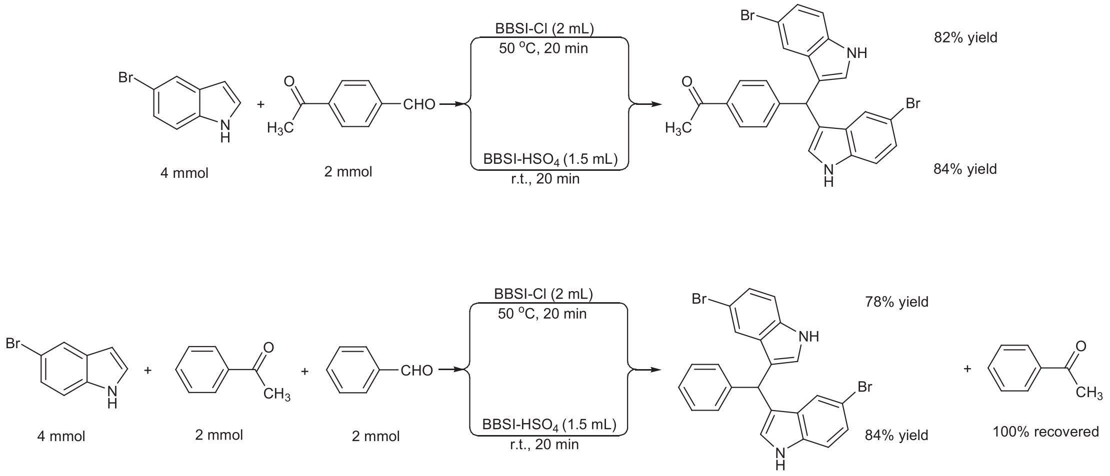
3.2. Instrumentation

The purity determination of the products was accomplished by GC–MS on an Agilent 6890GC/5973MSD analysis instrument under 70 eV



1h or 1p (8 mmol) **2 (2 mmol)** **3h** or **3p**

Scheme 4. Synthesis of di(bis(indolyl)methyl) benzene in the presence of **BBSI-Cl** and **BBSI-HSO$_4$** under optimized conditions.



Scheme 5. Chemoselectivity of the present method under optimized conditions.

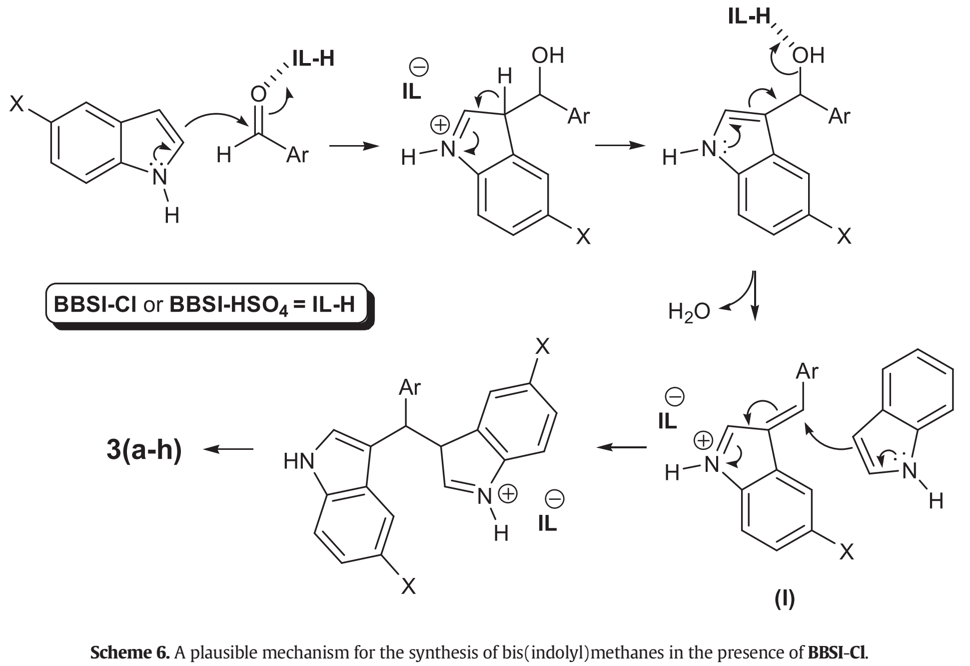
conditions. The FTIR spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat for liquid samples in the range of 4000–400 cm^{-1}. In all the cases the ^1H and ^{13}C NMR spectra were recorded with Bruker Avance III 600 MHz and 400 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Microanalyses were performed on a Perkin- Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The mass spectra of the products were recorded using an Agilent 6560 iFunnel Q–TOF LC–MS instrument.

*3.3. Synthesis of 1,1′-(1,4-Butanediyl)bis(imidazole) (**BBI**)*

Sodium hydride 60% dispersion in mineral oil (0.4 g, 10 mmol) was slowly added to a flask contain imidazole (0.68 g, 10 mmol) and ground at room temperature for 2 h. 1,4-Dichlorobutane (0.55 mL, 5 mmol) was added, and the mixture was stirred at room temperature overnight. The resulting liquid was poured into 5 mL of water. A white solid formed immediately which weighed 0.94 g (98%) after drying and had the following properties: mp 83–86 °C; IR (KBr): $\nu_{max} = 3384, 3111, 2925, 1669, 1505, 1463, 1440, 1394, 1378, 1281, 1238, 1108, 1081, 917, 824, 735, 730, 660, 628\ cm^{-1}$; ^1H NMR (600 MHz, DMSO d_6) $\delta = 7.61$ (s, 2H), 7.13 (t, $J = 1.2$ Hz, 2H), 6.88 (t, $J = 1.02$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 4, N-CH_2), 1.60–1.63 (m, 4, –CH_2CH_2–) ppm; ^{13}C NMR (150 MHz, DMSO d_6) $\delta = 137.66, 128.86, 119.68, 45.74, 28.13$ ppm; MS(ESI) *m*/*z*: calcd for $C_{10}H_{15}N_4^+$: 191.1, found: 191.1 and MS(ESI) *m*/*z*: calcd for $C_{10}H_{14}N_4Na^+$: 213.1, found: 213.1.

*3.4. Typical synthesis of 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride (**BBSI-Cl**)*

Chlorosulfonic acid (0.15 mL, 2 mmol) was dropwise added to 1,l′-(1,4-butanediyl)bis(imidazole) **BBI** (0.38 g, 2 mmol) in dry CH_2Cl_2 (2 mL). The reaction mixture was stirred at room temperature for 6 h, it formed two phases; the upper phase was decanted and excess of



Scheme 6. A plausible mechanism for the synthesis of bis(indolyl)methanes in the presence of **BBSI-Cl**.

Table 4
Comparison of the results obtained for the synthesis of **3a** in the presence of **BBSI-Cl** and **BBSI-HSO$_4$** with those afforded using some of the other ionic liquids.

Entry	Catalyst	Catalyst loading (%)	Temperature (°C)/solvent	Time (min)	Yield (%)	Ref.
1	(THA)(HSO$_4$)	2	r.t./solvent-free	10	90	[45]
2	[n-Pr$_2$NH$_2$][HSO$_4$]	10	Microwave (560 W)/EtOH	5	95	[46]
3	Sulfamic acid	10	r.t./MeOH	180	90	[47]
4	[hmim][HSO$_4$]	5	r.t./EtOH	60	97	[48]
5	SuSA	5	r.t./MeCN	45	96	[42]
6	Aminosulfonic acid	150	Ultrasound (25KHz, 250 W)/ EtOH & H$_2$O (N$_2$ atm)	30	93	[49]
7	[bmim][BF$_4$] or [bmim][PF$_6$]	2 mL	r.t./solvent-free	270	87	[49]
8	In(OTf)$_3$	5	r.t./[omim][PF$_6$]	15	90	[50]
9	**BBSI-Cl**	2 mL	50/solvent-free	20	91	This work
10	**BBSI-HSO$_4$**	1.5 mL	r.t./solvent-free	20	95	This work

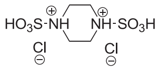
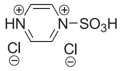
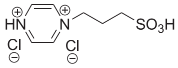
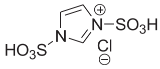
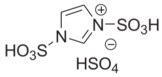
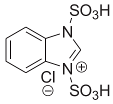
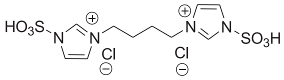
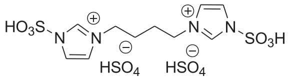
(THA)(HSO$_4$) = tris(hydroxymethyl)methane ammonium hydrogen sulfate; SuSA = Succinimide sulfonic acid.

solvent was removed under vacuum evaporation. The resulting colorless liquid was weighed 0.83 g (98%) after drying and had the following properties: IR (KBr): ν_{max} = 3401, 3144, 2926, 2854, 1626, 1579, 1548, 1455, 1408, 1116, 1048, 995, 878, 758, 635, 614, 588 cm^{-1}; ^{1}H NMR (600 MHz, DMSO d_6) δ = 9.16 (s, 2H), 7.79 (dd, *J* = 1.5 and 1.5 Hz, 2H), 7.68 (dd, *J* = 1.6 and 1.4 Hz, 2H), 4.26 (t, *J* = 5.9 Hz, 4H, NC$\underline{H_2}$), 1.81–1.77 (m, 4H, NCH$_2$C$\underline{H_2}$) ppm; ^{13}C NMR (150 MHz, DMSO d_6) δ = 135.6, 122.4, 120.4, 48.1, 26.7 ppm; MS(ESI) *m*/*z*: calcd for $C_{10}H_{15}N_4O_6S_2^+$: 351.0, found: 351.2 and MS(ESI) *m*/*z*: calcd for $C_{10}H_{17}N_4O_6S_2^+$: 353.0, found: 353.2.

3.5. Typical synthesis of 1,1′-butylenebis(3-sulfo-3H-imidazol-1-ium) hydrogen sulfate (BBSI-HSO$_4$)

Neat sulfuric acid (0.196 g, 2 mmol) was dropwise added to **BBSI-Cl** (0.85 g, 2 mmol) in dry CH$_2$Cl$_2$ (2 mL). The reaction mixture was stirred at 50 °C for 6 h under a continuous flow of nitrogen to remove the hydrogen chloride gas produced during the reaction which formed two phases; the upper phase was decanted and excess of solvent was removed under vacuum evaporation. The resulting yellow viscous liquid was weighed 1.06 g (97%) after drying and showed the following properties: IR (KBr): ν_{max} = 3500–3350, 3151, 2878, 1677, 1580, 1548, 1454, 1409, 1143, 1087, 1017, 861, 751, 620, 568 cm^{-1}; ^{1}H NMR (600 MHz, DMSO d_6) δ = 14.32 (br s, 2H), 9.11 (s, 2H), 7.77 (dd, *J* = 1.6 and 1.5 Hz, 2H), 7.66 (dd, *J* = 1.6 and 1.4 Hz, 2H), 4.26 (t, *J* = 5.7 Hz, 4H, NC$\underline{H_2}$), 1.80–1.77 (m, 4H, NCH$_2$C$\underline{H_2}$–) ppm; ^{13}C NMR (150 MHz, DMSO d_6) δ = 135.8, 122.5, 120.4, 48.1, 26.7 ppm; MS(ESI) *m*/*z*: calcd for $C_{10}H_{15}N_4O_6S_2^+$: 351.0, found: 351.2 and MS(ESI) *m*/*z*: calcd for $C_{10}H_{17}N_4O_6S_2^+$: 353.0, found: 353.2.

Table 5
Comparison of result obtained for the synthesis of 3,3′-(4-chlorophenylmethylene)bis(1*H*-indole) in the presence of some sulfonic-functionalized ionic liquid containing mono- and di- cationic nucleus with **BBSI-Cl** and **BBSI-HSO$_4$**.[a]

Entry	IL as solvent-catalyst	Abbreviation	Yield (%)
1		PiS-Cl	68
2		PzS-Cl	62
3		PzPS-Cl	74
4		DSI-Cl	62
5		DSI-HSO$_4$	67
6		DSBI-Cl	64
7		BBSI-Cl	76
8		BBSI-HSO$_4$	96

[a] Reaction conditions: 4-chlorobenzaldehyde (**1d**) (2.0 mmol), indole (4.0 mmol), IL (2 mL), reaction time (20 min), room temperature.

3.6. Physical and spectral data of some products

1,4-bis(di(1H-indol-3-yl)methyl)benzene (***3h***): Mp = 245–247 °C, Lit. Mp = 246.5–248 °C [55]; FTIR (KBr) ν_{max} = 3408, 3051, 1615, 1455, 1417, 1337, 1215, 1092, 1010, 738 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.40 (d, *J* = 7.6 Hz, 4H),7.18 (s, 4H), 7.15(t, *J* = 7.6 Hz, 4H), 7.08–7.05 (m, 8H), 6.67 (s, 4H), 5.79 (s, 4H), 5.69 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ = 141.5, 136.5, 128.6, 127.0, 123.8, 121.7, 119.9, 119.2, 118.9, 111.4, 39.9 ppm; Anal. Calcd. for $C_{40}H_{30}N_4$: C, 84.78; H, 5.34; N, 9.89; Found: C, 84.73; H, 5.39; N, 9.86; HRMS (ESI): Calcd. For $[M-H]^-$ $C_{40}H_{29}N_4$: 565.2398; Found 565.2378. ^{1}H NMR and ^{13}C NMR were in agreement with that published in the literature [38].

3,3′-((4-methylphenyl)methylene)bis(5-bromo-1H-indole) (***3j***): Mp = 210–212 °C;, Lit. Mp = 212–214 °C [56]; FTIR (KBr) ν_{max} = 3421, 3024, 2922, 2864, 1602, 1591, 1514, 1475, 1448, 1342, 1284, 1201, 1170, 1110, 835, 752, 732 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.94 (s, 2H), 7.46 (d, *J* = 1.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.19–7.05 (m, 6H), 6.58 (d, *J* = 1.6 Hz, 2H), 5.68 (s, 1H), 2.31 (s,3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ = 140.1, 136.0, 135.4, 129.2, 128.8, 128.4, 125.0, 124.9, 122.4, 119.4, 112.8, 39.6, 21.2 ppm; Anal. Calcd. for $C_{24}H_{18}Br_2N_2$: C, 58.33; H, 3.67; N, 5.67; Found: C, 58.29; H, 3.65; N, 5.61. ^{1}H NMR and ^{13}C NMR were in agreement with that published in the literature [56].

3,3′-((furan-2-yl)methylene)bis(5-bromo-1H-indole) (***3n***): Mp = 181–183 °C; FTIR (KBr) ν_{max} = 3410, 2932, 2825, 1625, 1581, 1510, 1480, 1451, 1442, 1340, 1290, 1205, 1172, 1105, 1045, 920, 835, 790, 752, 732 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.94 (s, 2H), 7.26 (m, 2H), 6.91 (s, 2H), 6.83–6.79 (m, 5H), 6.72 (s, 1H), 6.27 (d, *J* = 4.0 Hz, 1H), 5.81 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ = 160.2, 135.7, 131.0, 128.6, 127.9, 124.2, 113.6, 113.5, 112.8, 110.8, 83.4, 44.4 ppm; Anal. Calcd. for $C_{21}H_{13}Br_2N_2O$: C, 48.96; H, 2.54; N, 8.16; Found: C, 48.91; H, 2.50; N, 8.11.

1,4-bis(di(5-bromo-1H-indol-3-yl)methyl)benzene (***3p***): Mp = 210 °C (dec.), Lit. Mp = 210 °C (dec.) [39]; FTIR (KBr) ν_{max} = 3400, 3050, 2840, 1679, 1454, 1330, 1217, 1090, 1012, 558 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.07 (s, 4H), 7.44 (s, 4H), 7.27–7.18 (m, 8H), 7.09 (s, 4H), 6.39 (s, 4H), 5.64 (s, 2H) ppm; ^{13}C NMR (100 MHz,

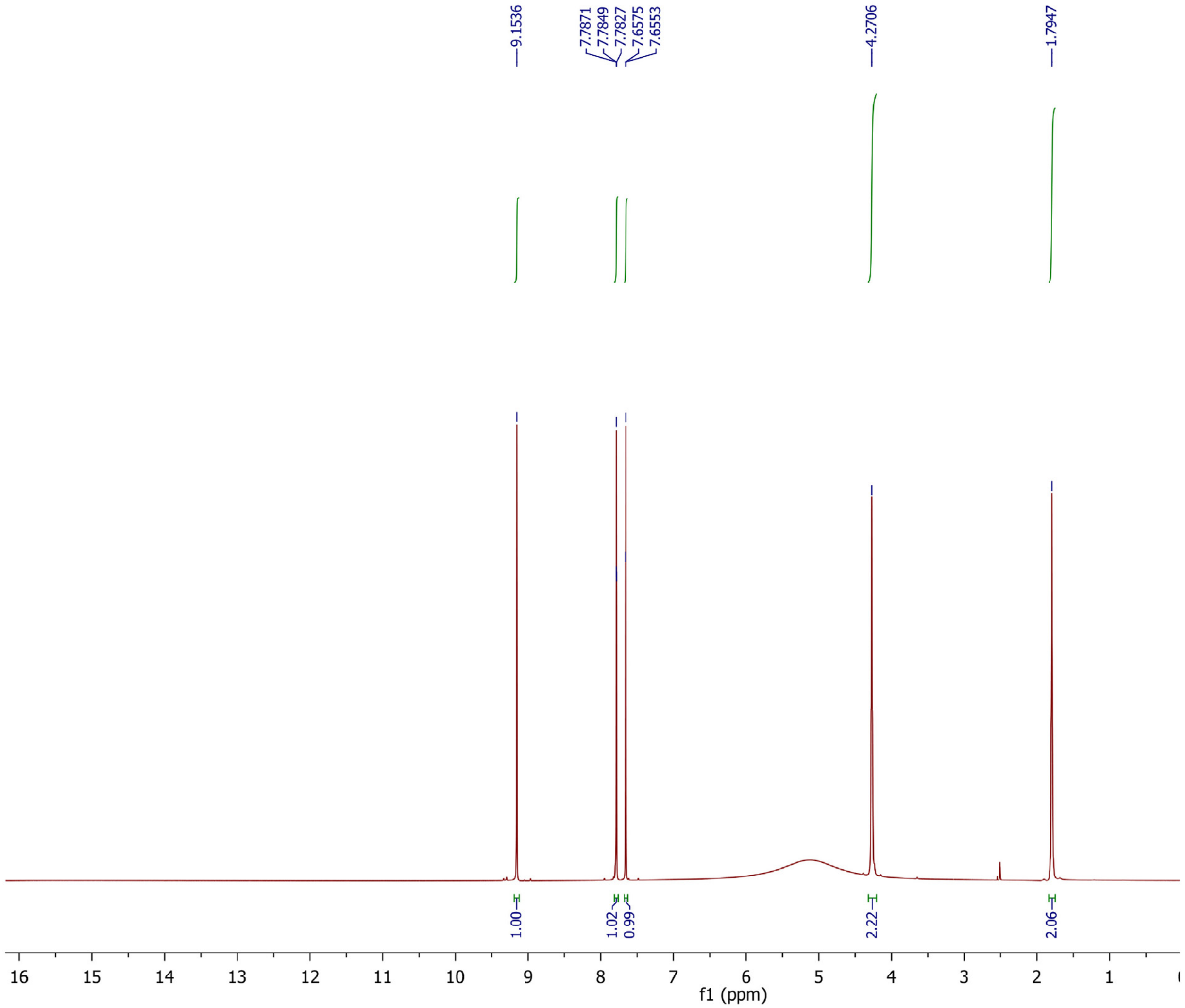


Fig. 7. ^{1}H NMR Spectra of reused **BBSI-Cl** after the third run.

CDCl$_3$) δ = 141.1, 135.2, 127.9, 124.9, 124.5, 122.0, 118.7, 112.1, 112.2, 39.4 ppm; Anal. Calcd. for $C_{40}H_{26}Br_4N_4$: C, 54.45; H, 2.97; N, 6.35; Found: C, 54.41; H, 2.95; N, 6.32; HRMS(ESI): Calcd. For $[M - H]^-$ $C_{40}H_{25}Br_4N_4$: 876.8818; Found 876.8804. IR, ^{1}H NMR and ^{13}C NMR were in agreement with that published in the literature [41].

1-(4-(bis(5-bromo-1H-indol-3-yl)methyl)phenyl)ethanone (***3q***): Mp: 115–117 °C; FTIR (KBr) ν_{max} = 3425, 2931, 2851, 1671, 1600, 1462, 1265, 1204, 1165, 1102, 886, 783 cm^{-1}; ^{1}H NMR (400 MHz, DMSO *d$_6$*) δ = 11.11 (s, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 9.2 Hz, 2H), 7.44 (s, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.16–7.13 (m, 2H), 6.91 (d, *J* = 2.4 Hz, 2H), 5.97 (s, 1H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO *d$_6$*) δ = 198.4, 148.9, 135.5, 135.3, 128.8, 128.6, 128.4, 125.1, 124.8, 122.0, 117.9, 112.8, 112.7, 39.9, 26.62 ppm; Anal. Calcd. for $C_{25}H_{18}Br_2N_2O$: C, 57.50; H, 3.47; N, 5.36; Found: C, 57.42; H, 3.51; N, 5.29.

4. Conclusion

In summary, two new binuclear sulfonic-functionalized acidic ionic liquid as a task-specific ionic liquid was prepared and their structure was characterized by FTIR, MS, ^{1}H and ^{13}C NMR; then some physical properties and pH of the solution of ionic liquids were determined in water. Its dual solvent-catalytic property was proved for the synthesis of bis(indolyl)methanes under mild conditions. The effect of the presence of the four-carbon spacer and acidic anion on the catalytic activity of two ionic liquids were studied in comparison with some previously reported sulfonic-functionalized ILs which proved the superiority of binuclear ionic liquids containing acidic counter anion in comparison to mononuclear with a nonacidic anion. The current protocol has the advantages such as simple experimental and sustainable procedure, good yield of the desired products within short reaction times, and recyclability of ionic liquids. Their application for the synthesis of symmetric bis(indolyl)methanes has highlighted the importance of binuclear and spacer of task-specific ionic liquids as dual solvent-catalyst in organic chemistry, and we hope that our work will encourage further research in this area.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

This work was supported by a High Impact Research Grant (No. RP025A/B/C-14AET) for Scientific Research from University of Malaya, Malaysia. The authors are grateful to staff members in the Analytical and Testing Center of Research House of Professor Reza and Malaya University for partial support.

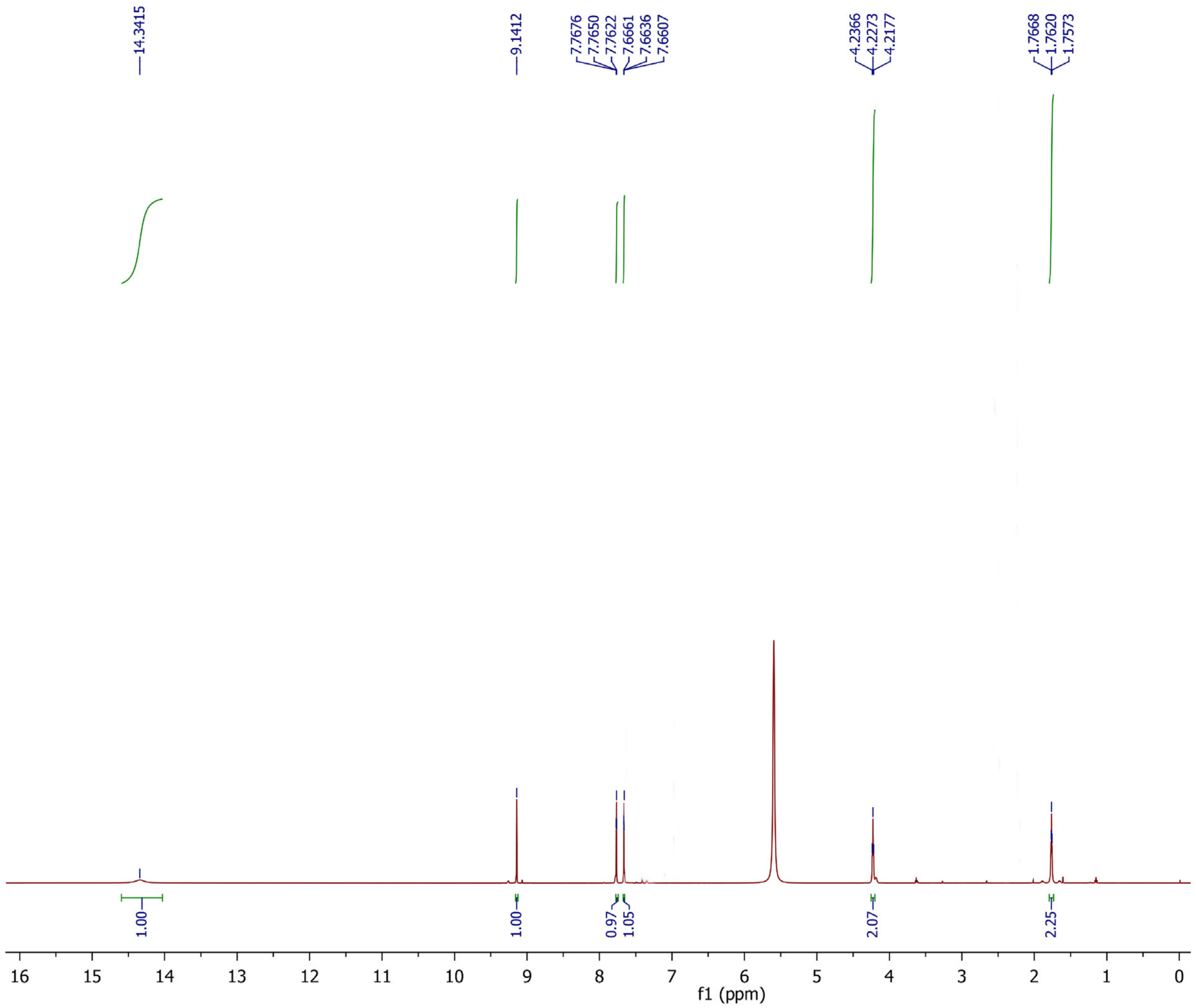


Fig. 8. ^{1}H NMR Spectra of reused **BBSI-HSO$_4$** after the third run.

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