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3-Methyl-1-sulfonic Acid Imidazolium Mesylate as a Novel, Highly Effective and Dual-functional Catalyst for the Solvent-free Production of Bis-coumarins

A. Kargar-Dolatabadi, S.S. Sajadikhah*, A. Zare and A. Razaghi
Department of Chemistry, Payame Noor University, P. O. Box: 19395-3697, Tehran, Iran
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A novel ionic liquid entitled 3-methyl-1-sulfonic acid imidazoliummesylate ([Msim][OMs]) was synthesized and characterized using FT-IR, ^{1}H NMR, ^{13}C NMR andmass spectra. This ionic liquid was employed as a dual-functional catalyst for the preparation of bis-coumarins *via* the one-pot pseudo three-component reaction of 4-hydroxycoumarin (2 eq.) and arylaldehydes (1 eq.) under solvent-free and relatively mild conditions. Owing to dual-functionality of [Msim][OMs] (having acidic and basic sites), it could act as a highly effective catalyst for the reaction. Additionally, an attractive mechanism based on dual-functionality of the catalyst was proposed.

Keywords: Ionic liquid, 3-Methyl-1-sulfonic acid imidazolium mesylate ([Msim][OMs]), Bis-coumarins, Dual-functional catalyst, Solvent-free

INTRODUCTION

The specific properties of ionic liquids (ILs) are mainly attributed to their cationic and anionic moieties, and length of the alkyl groups in the cation. The physical and chemical parameters of ILs, such as density, viscosity, solubility, melting point and catalytic activity can be adjusted by modifying the chemical structure of their cations and anions. The main features of these compounds include light vapor pressure, non-inflammability, high dissolution, low melting point, thermal and chemical stability, low toxicity and fluidity in a wide range of temperatures [1-10]. ILs could be especially utilized as a solvent, reagent and catalyst in organic synthesis [3-10].

Carrying out organic transformations in solvent-free conditions has often various benefits relative to performing them in organic solvents; these benefits consist of no need for collecting and distilling the solvent, consuming lower energy, enhancing effectiveness of reaction, decreasing reaction time, being more economic, and agreement with green chemistry principles [11-14].

Coumarin moiety is found in a variety of pharmaceutical, biological and industrial compounds. The compounds bearing this core possess miscellaneous pharmaceutical and biological activities, such as anti-cancer [15], antibacterial [15], antinociceptive [15], anti-HIV [16,17], cytotoxicity, enzyme and urease inhibitory [18-20], antimicrobial [21], antioxidant [21] and anticoagulant [22] properties. Coumarin derivatives have also optical and fluorescence emission activities [23-25]. An important group of coumarin-containing materials is bis-coumarins produce by the one-pot pseudo three-component reaction of 4-hydroxycoumarin (2 eq.) and aldehydes (1 eq.); some catalysts have been reported for this synthesis [26-35]. However, in spite of their potential effectiveness, many of these catalysts have some or at least one of the following disadvantages: prolonged reaction times, moderate yields, utilization of volatile organic solvents as reaction media, high reaction temperature and poor compliance with green chemistry principles.

In this research, we have prepared a novel ionic liquid entitled 3-methyl-1-sulfonic acid imidazolium mesylate([Msim][OMs]), and characterized using FT-IR,^{1}H NMR, ^{13}C NMR and mass spectral analysis. Subsequently, we have utilized [Msim][OMs] as a highly effectual and dual-functional catalyst for the one-pot pseudo three-

*Corresponding author. E-mail: sssajadi@pnu.ac.ir

component condensation of 4-hydroxycoumarin (2 eq.) and aldehydes (1 eq.) to provide bis-coumarins. Our catalyst has none of the above-mentioned drawbacks at all.

EXPERIMENTAL

General

All starting materials and solvents were obtained from Merck, Fluka or Acros Chemical Companies. The known compounds were identified by comparing their melting points/spectroscopic data with those reported in the literature. Monitoring progress of the reactions was achieved by thin layer chromatography (TLC). The FT-IR spectra were obtained on a JASCO FT-IR-600 plus spectrometer. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (250 or 400 MHz) and ^{13}C NMR (62.5 or 100 MHz) spectra were recorded on a Bruker Avance DPX, FT-NMR spectrometer. Mass spectra were obtained by Shimadzu GC-MS-QP 1100 EX model.

Preparation of 3-Methyl-1-sulfonic Acid Imidazoliummesylate ([Msim][OMs])

A round-bottomed flask (100 ml) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry CH_2Cl_2 (30 ml), and then, chlorosulfonic acid (0.594 g, 5.1 mmol) was added dropwise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min, maintained for 5 min, and CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 10 ml) and dried under vacuum to give 3-methyl-1-sulfonic acid imidazolium chloride ([Msim][Cl]) as a viscous colorless oil [6]. Then, methanesulfonic acid (0.481 g, 5 mmol) was added dropwise to [Msim][Cl] (0.993 g, 5 mmol) over a period of 3 min at room temperature. The resulting mixture was stirred for 12 h at room temperature, and 2 h at 60 ºC to give [Msim][OMs] as a viscous pale yellow liquid in a quantity yield. FT-IR (KBr, cm^{-1}): ν = 864, 1045, 1180, 2959,3147, 2000-3600; ^{1}H NMR (250 MHz, DMSO-d$_6$):δ (ppm) = 2.42 (s, 3H), 3.85 (s, 3H), 7.62-7.67 (m, 2H), 9.01 (s, 1H), 14.25 (br., 1H); ^{13}C NMR (62.5MHz, DMSO-d$_6$): δ (ppm) =35.8, 40.1, 120.1, 123.6, 136.2; Mass(EI, 70 eV): *m/z*(%) = 258 (M^+, 2), 259 (M^+ + 1, 1).

General Procedure for the Synthesis of Bis-coumarins

A mixture of compounds consisting of 4-hydroxylcoumarin (0.324 g, 2 mmol), arylaldehyde (1 mmol) and [Msim][OMs] (0.013 g, 0.05 mmol) was firstly stirred magnetically at 70 ºC, and after solidification of the reaction mixture, it was stirred by a small rod at the same temperature. After completion of the reaction (as monitored by TLC eluted by EtOAc/*n*-hexane: 1/3), the reaction mixture was cooled to room temperature, and the resulting precipitate was recrystallized from EtOH (95%) to give the pure product.

Selected Spectral Data of the Products

Compound c. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 6.31 (s, 1H, methineCH), 7.13 (d, J = 8.0Hz, 2H, H$_{Ar}$), 7.31-7.42 (m, 6H, H$_{Ar}$), 7.60 (t, J = 7.6, Hz, 2H, H$_{Ar}$), 7.91 (d, J = 7.8 Hz, 2H, H$_{Ar}$), 10.38 (br., 2H, 2OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 36.2, 104.2, 116.4, 118.8, 118.9, 124.1, 124.4, 129.6, 131.3, 132.3, 140.7, 152.8, 165.1, 166.4.

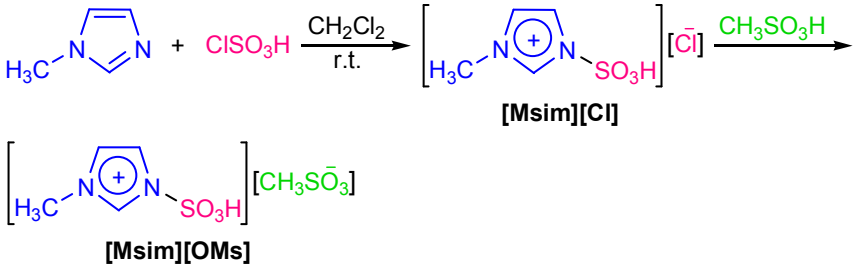
Compound h. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 5.06 (s, 1H, CH$_2$), 6.32 (s, 1H, methineCH), 6.90 (d, J = 8.4 Hz, 2H, H$_{Ar}$), 7.08(d, J = 8.4 Hz, 2H, H$_{Ar}$), 7.30-7.46 (m, 9H, H$_{Ar}$), 7.61 (t, J = 7.2 Hz, 2H, H$_{Ar}$), 7.93 (d, J = 7.6 Hz, 2H, H$_{Ar}$), 9.48 (br., 2H, 2OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 35.7, 69.6, 104.7, 114.8, 116.4, 118.6, 124.2, 124.4, 128.1, 128.2, 128.9, 129.0, 132.3, 132.4, 137.7, 152.7, 156.9, 165.3, 166.8.

Compound k. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 3.60 (s, 6H, 2CH$_3$), 3.65 (s, 3H, CH$_3$), 6.26 (s, 1H, methine CH), 6.46 (s, 2H, H$_{Ar}$), 7.31-7.37 (m, 4H, H$_{Ar}$), 7.59 (t, J = 8.4 Hz, 2H, H$_{Ar}$), 7.92 (d, J = 7.9 Hz, 2H, H$_{Ar}$); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 36.8, 56.5, 60.4, 104.9, 105.1, 116.5, 117.9, 124.4, 124.5, 132.4, 135.6, 136.7, 152.7, 153.1, 165.2, 165.3.

RESULTS AND DISCUSSION

Characterization of the Catalyst

3-Methyl-1-sulfonic acid imidazolium mesylate ([Msim][OMs]) was prepared by the reaction of 1-methylimidazole and chlorosulfonic acid to give [Msim][Cl], and then the reaction of [Msim][Cl] with



Scheme 1. Preparation of [Msim][OMs]

Table 1. The FT-IR Data of [Msim][OMs]

Peak (cm^{-1})	Related bond or functional group
864	N-S symmetric stretching
1045	S-OH bending
1180	S=O stretching of mesylate
2959	C-H stretching of methyl groups
3147	C-H stretching of imidazolium
2000-3600	OH group of the SO_3H

methanesulfonic acid (Scheme 1).

[Msim][OMs] was characterized by analyzing its FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectral data.

In the FT-IR spectrum (Fig. S1, Supplementary Material), the peaks related to the expected bonds and functional groups in [Msim][OMs] were observed; the main IR data are summarized in Table 1.

In the ^{1}H NMR spectrum of [Msim][OMs] (Fig. 1), six peaks were observed. Analysis of the spectrum is given in Table 2.

There are five kinds of carbon in [Msim][OMs]. The ^{13}C NMR spectrum of [Msim][OMs]is shown in Fig. 2, and interpretation of the spectrum is summarized in Table 3.

In the mass spectrum of [Msim][OMs] (Fig. 3), the peaks observed at *m/z* 258 and 259 are related to the molecular mass (M^+) and (M^++1), respectively.

Examining the Catalytic Activity of [Msim][OMs] for the Preparation of Bis-coumarins

After full characterization of [Msim][OMs], its catalytic activity was examined for the reaction of 4-hydroxy-coumarin with arylaldehydes to give bis-coumarins. For doing so, the condensation of 4-hydroxycoumarin (2 mmol) and benzaldehyde (1 mmol) was selected as a model (Scheme 2) .For acquiring the optimum reaction conditions in terms of the catalyst amount, temperature and solvent, the model reaction was checked in the presence of different mol% (2.5, 5 and 7) of [Msim][OMs] at a range of 60-75 ºC under solvent-free conditions, and also in some refluxed solvents (ethanol, methanol, acetonitrile, and methylene chloride). The reasonable reaction time and yield were gained when the reaction was carried out using 5 mol% of the ionic liquid at 70 ºC in the absence of solvent (time:

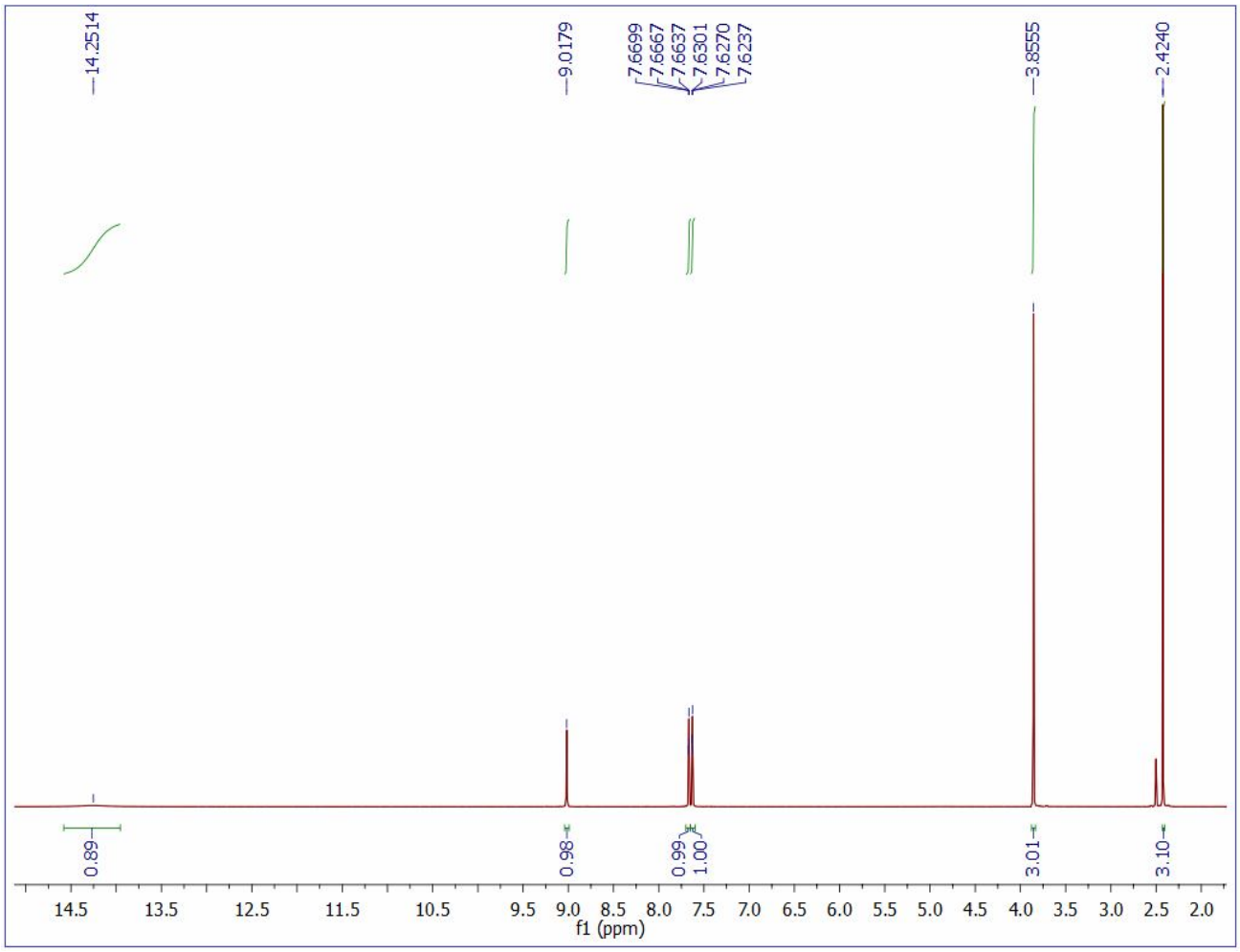
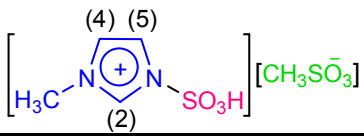


Fig. 1. The ^{1}H NMR spectrum of the catalyst.

Table 2. Analyzing the ^{1}H NMR Data of 3-Methyl-1-sulfonic Acid Iimidazolium Mesylate



Chemical shift (ppm)	2.42	3.85	7.62-7.67	9.01	14.25
Integral	3.10	3.01	1.99	0.98	0.89
Splitting pattern	Singlet	Singlet	Multiplet	Singlet	Broad
Hydrogen kind	CH_3-S	CH_3-N	H-4 and H-5 of imidazolium	H-2 of imidazolium	SO_3H
Hydrogen number	3	3	2	1	1

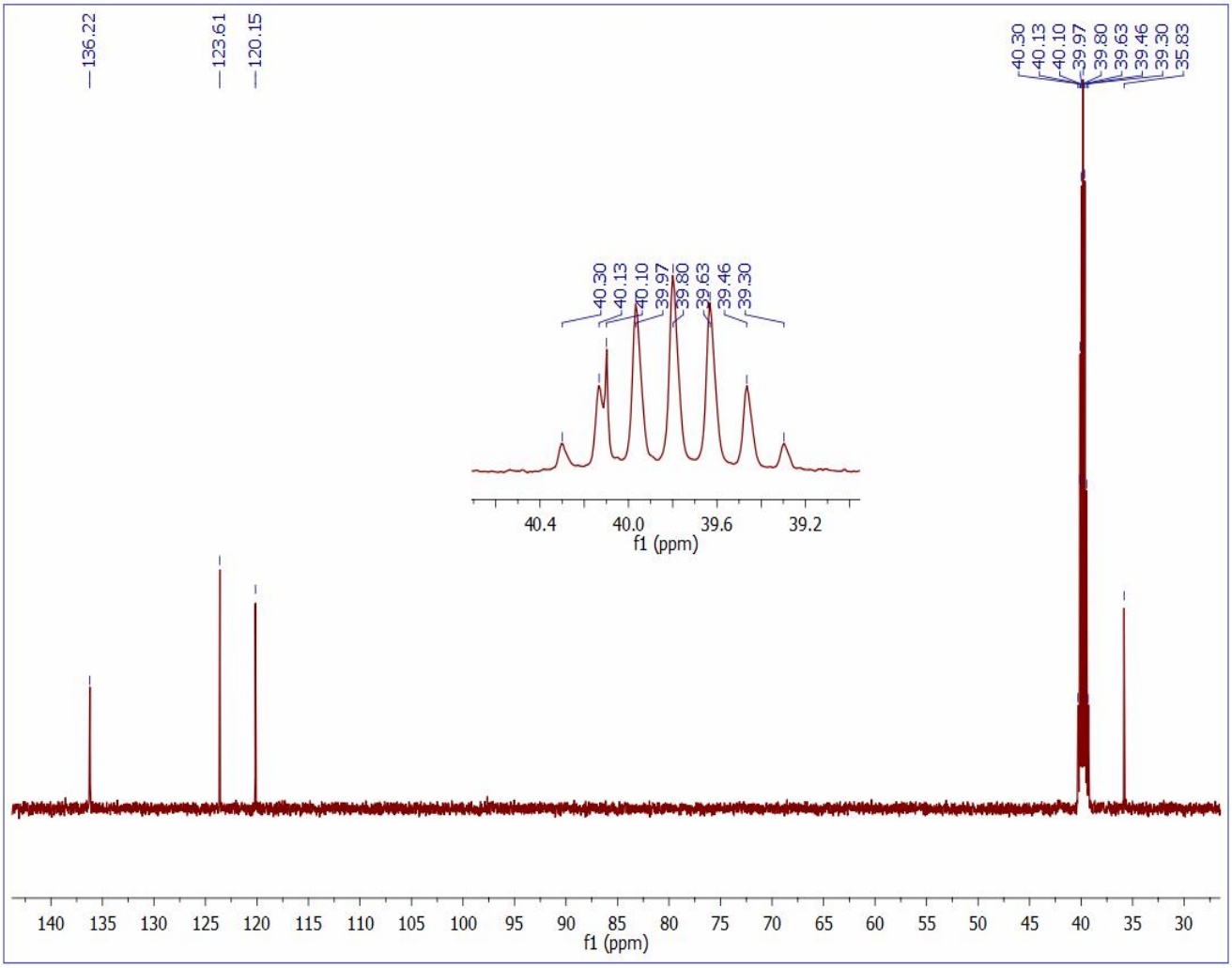
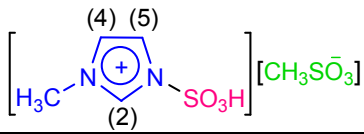


Fig. 2. The ^{13}C NMR spectrum of [Msim][OMs].

Table 3. Analysis of the ^{13}C NMR Data of [Msim][OMs]



Chemical shift (ppm)	35.8	39.3-40.3	40.1	120.1	123.6	136.2
Carbon kind	CH_3-N	DMSO-d_6 (solvent)	CH_3-S	C-4 of imidazolium	C-5 of imidazolium	C-2 of imidazolium

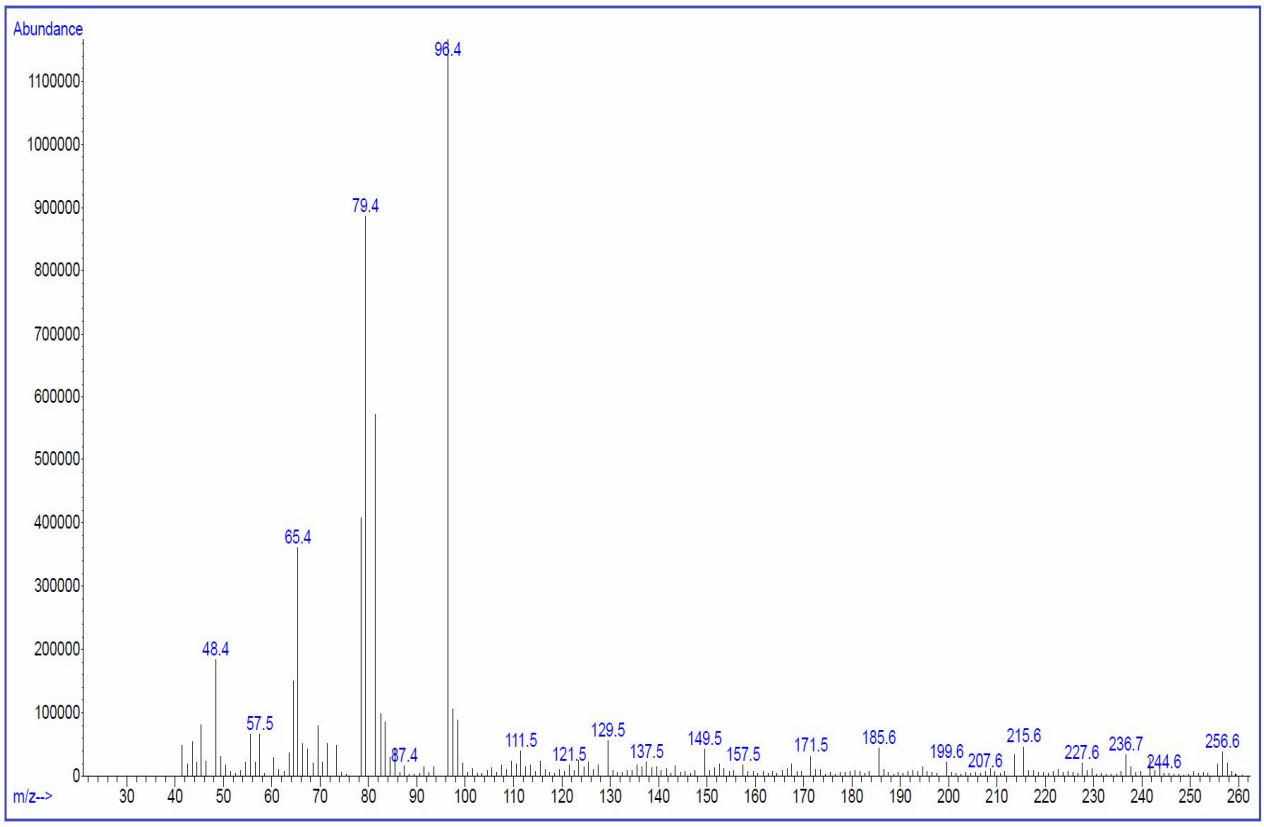
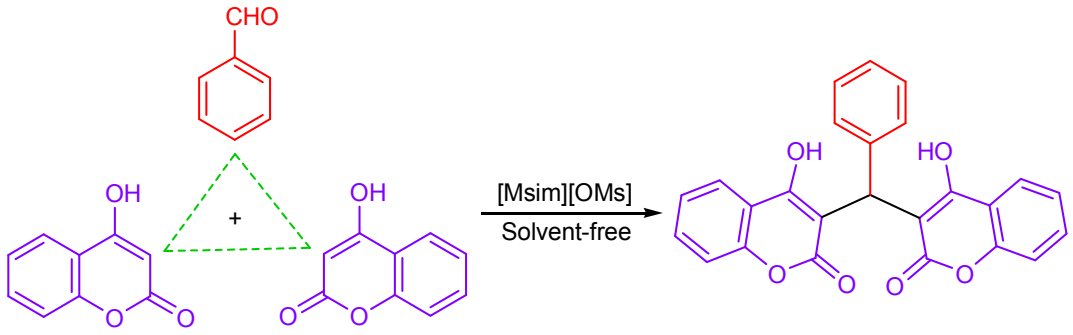


Fig. 3. The mass spectrum of the novel ionic liquid.

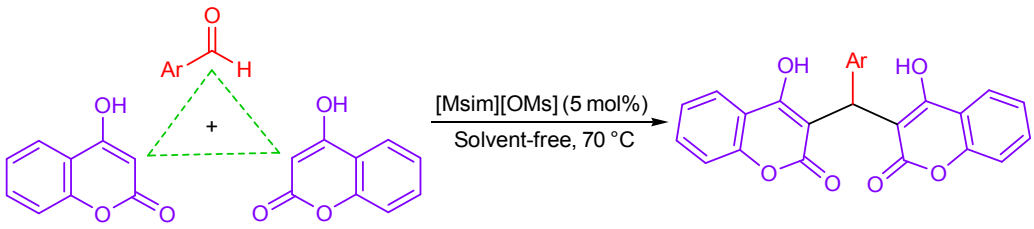


Scheme 2. The model reaction.

10 min; yield: 97%).

In order to show the effectiveness and generality of the ionic-liquid catalyst for the production of bis-coumarins, the optimum conditions were applied for the reaction of 4-hydroxycoumarinand miscellaneous arylaldehydes; the obtained results are displayed in Table 4. As it is obvious from the table, [Msim][OMs] was highly effective and general catalyst for the synthesis; since the bis-coumarins were produced in high yields and short reaction times in the case of benzaldehyde, and arylaldehydes bearing halogens,

Table 4. The Application of [Msim][OMs] as a Catalyst for the Production of Bis-coumarins



Product	Ar	Time (min)	Yield (%)[a]	M.p. (ºC) [lit.]
a	C_6H_5	10	97	232-234 (230-232) [35]
b	2-BrC_6H_4	10	91	261-263 (259-261) [30]
c	4-BrC_6H_4	10	96	266-268 (265-266) [34]
d	4-FC_6H_4	15	95	214-216 (213-215) [35]
e	2-$NO_2C_6H_4$	20	93	195-197 (198-200) [27]
f	3-$NO_2C_6H_4$	20	98	213-215 (214-215) [27]
g	4-$NO_2C_6H_4$	15	98	234-236 (232-234) [31]
h	4-$PhCH_2OC_6H_4$	60	87	181-183(177-179) [28]
i	4-$CH_3OC_6H_4$	15	95	244-246 (246-248) [35]
j	4-$CH_3C_6H_4$	25	94	270-271 (268-270) [34]
k	3,4,5-$(MeO)_3C_6H_2$	10	91	242-244 (239-240) [30]

electron-withdrawing and electron-releasing substituents on different positions of the aromatic ring.

To show the merit of our catalyst with respect to the reported catalysts for the preparation of bis-coumarins, the results of these catalysts on the reaction of 4-hydroxycoumarin with benzaldehyde are shown in Table 5. As this table indicates, [Msim][OMs] is superior in terms of the reaction time, yield, temperature or conditions.

The SO_3H group of [Msim][OMs] is acidic, and mesylate is basic (weak base); moreover, H-2 of imidazolium has a weak acidic property (see Fig. 4); thus, the ionic liquid can especially act as an effective catalyst for organic transformations which need both acidic and basic catalysts simultaneously; *e.g.*, the synthesis of bis-coumarins. This topic has been displayed in the reaction mechanism (Scheme 3). The roles of [Msim][OMs] in the reaction consists of: (i) accelerating nucleophile attacks to carbonyls through activating them by the SO_3H group (steps 1 and 3), (ii) removing H_2O by help of the acidic group (step 2), (iii) accelerating tautomerization by SO_3H (step 4), and (iv) activation of nucleophile by mesylate (steps 1 and 3). The mechanism is supported by the literature [26-28].

CONCLUSIONS

Briefly, we have introduced 3-methyl-1-sulfonic acid

Table 5. Comparison of the [Msim][OMs] Results with the Reported Catalysts for the Synthesis of Bis-coumarin

Catalyst	Conditions	Time (min)	Yield (%)	Ref.
[Msim][OMs]	Solvent-free, 70 ºC	10	97	-
Fe_3O_4@SiO_2@VB1-Ni^{2+}	Solvent-free, 110 ºC	30	95	[26]
[MIM$(CH_2)_4SO_3H$][HSO_4][a]	Solvent-free, 80 ºC	30	92	[27]
CuO-CeO_2nanocomosite	H_2O, reflux	20	93	[28]
Phthalimide-*N*-sulfonic acid	Solvent-free, 80 ºC	10	96	[29]
Isatin-*N*-sulfonic acid	Solvent-free, 85 ºC	10	96	[29]
Melamine trisulfonic acid	H_2O, 80 ºC	20	95	[30]
Fe_3O_4@SiO_2@$(CH_2)_3$-Im-SO_3H	Solvent-free, 100 ºC	12	93	[31]
Trityl bromide	Solvent-free, 100 ºC	20	92	[31]
[Pyridine-SO_3H]Cl	Solvent-free, 80 ºC	14	88	[33]
Catalyst-free	Ethylene glycol, 90 ºC	90	84	[34]
Sodium dodecyl sulfate	H_2O, 60 ºC	150	90	[35]

[a]3-Methyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate.

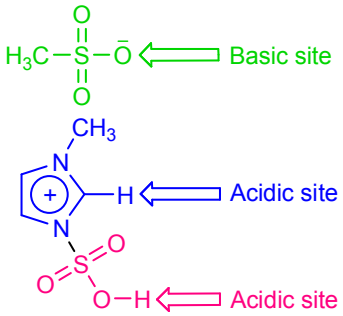


Fig. 4. The acidic and basic sites of [Msim][OMs].

imidazolium mesylate as a catalyst for organic reactions, especially for ones requiring both acidic and basic catalysts simultaneously; in this regard, we have used [Msim][OMs] to promote the reaction of 4-hydroxycoumarin and arylaldehydes leading to bis-coumarins. This protocol has several advantages, consisting of effectiveness, generality, performing the reaction in the absence of solvent, high yields, mild conditions, easy workup, short reaction times, relatively simple procedure for the catalyst synthesis, and good compliance with green chemistry principles.

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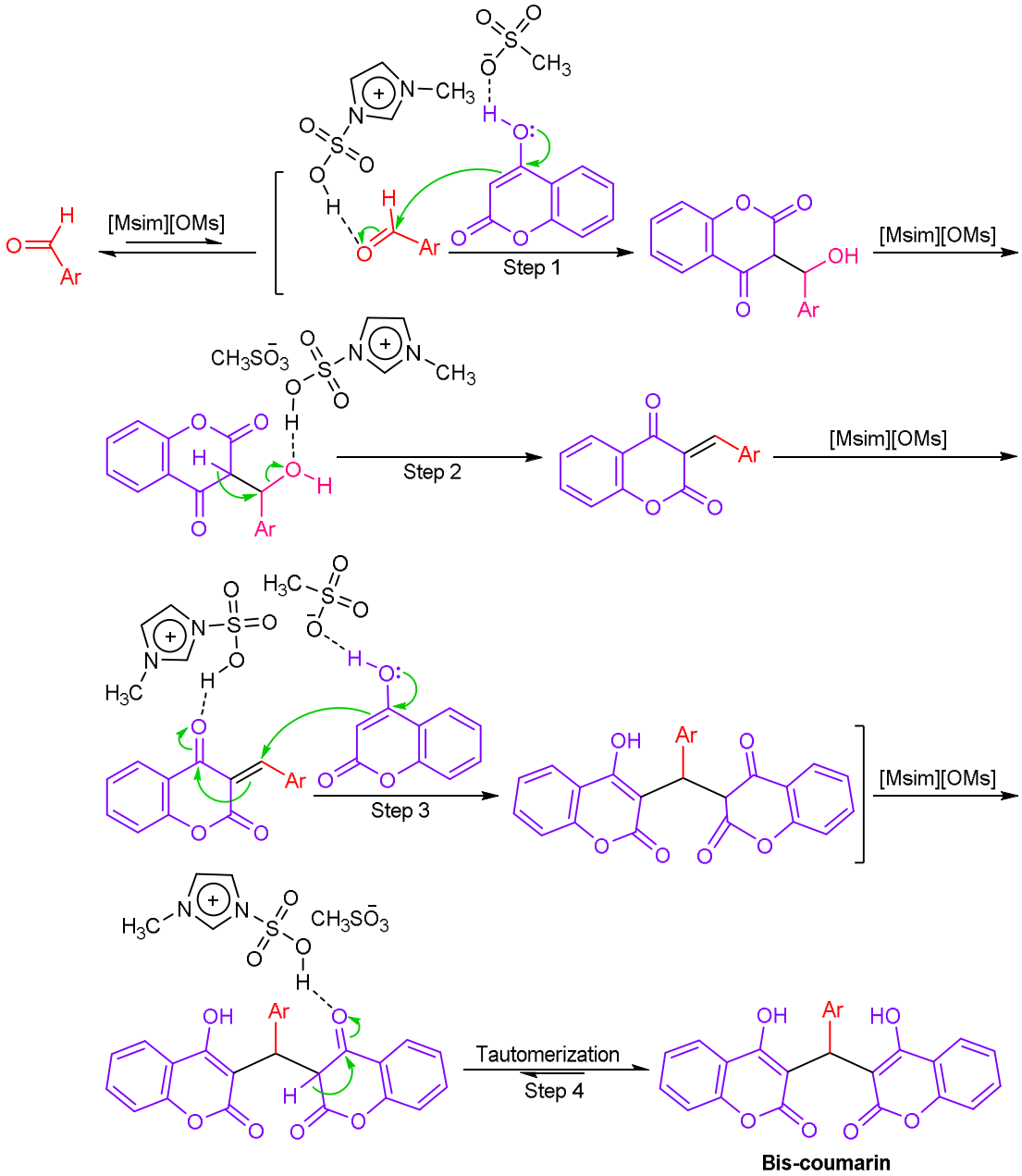

Scheme 3. The proposed mechanism for the synthesis of bis-coumarins

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