

Room Temperature Synthesis of Mequinol by Using Ionic Liquids as Homogeneous Recyclable Catalysts

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ABSTRACT: For synthesis of Mequinol (4-methoxy phenol), two acidic ionic liquids based on imidazolium cation (BMSIL and IMSIL) synthesized and characterized with FT-IR, ¹H NMR and CHNS analyses. Then, the Baeyer–Villiger oxidation of *para*-anisaldehyde was studied with these ionic liquids, as the catalysts. The results showed that the BMSIL with more Brønsted acidic functions had higher catalytic activity than IMSIL and even sulfuric acid at room temperature. Furthermore, the different reaction parameters were studied and maximum conversion (99%) and selectivity (95%) of Mequinol was observed by using 5% BMSIL as catalyst, H₂O₂ (30% solution) as oxidant, Methanol as solvent at 3.5 h, and room temperature condition. Also, we investigated the effect of different substituents in the aromatic ring of benzaldehyde and various solvents on the catalytic activity of BMSIL ionic liquid as the best catalyst in the oxidation of aromatic aldehydes. The results show that the protic solvent and electron-donating substituents in *para* position of benzaldehyde favor the phenol product.

KEYWORDS: Mequinol; Baeyer–Villiger oxidation; Acid catalyst; Ionic liquid.

INTRODUCTION

Substituted phenols are important intermediates for drugs, agrochemicals, and dyes. For example, Mequinol (4-methoxy phenol) is used as polymerization inhibitors, antioxidants for foods and cosmetics [1,2]. It is also used in combination with the drug tretinoin in the treatment of liver spots and used alone as a topical drug for medical depigmentation [3,4].

Classical synthesis of this kind of phenols can be performed by monoalkylation of hydroquinone with alkylating agents such as the dialkyl sulfate, haloalkanes, and alcohols, usually in the presence of acid or base catalytic conditions [5-8]. However, di-alkylation can also happen during

the reaction and decrease the yield of the desired product. Alternatively, the Baeyer–Villiger oxidation of alkoxy benzaldehydes such as *para*-anisaldehyde (4-methoxybenzaldehyde) can be another way to the synthesis of the mono-alkoxyphenols. Barton et al. synthesized Mequinol in high yield when 4-hydroxybenzaldehyde or acetophenone was treated with a methanol as an alkylating agent and ammonium peroxydisulfate as oxidant with a catalytic amount of sulfuric acid at 60 °C [9]. Also, the Baeyer–Villiger oxidation of *para*-anisaldehyde with different oxidants and catalysts such as *meta*-chloroperbenzoic acid (mCPBA) [10], monopersuccinic

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acid [11], H_2O_2 /seleninic acid [12], $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ [13], H_2O_2 /formic acid [14] and H_2O_2 /Sn-Beta zeolite [1] have been studied. There is much encouragement to find new environmentally friendly catalysts and processes for converting the substituted aromatic aldehydes to the corresponding phenols.

In recent years, application of ionic liquid increased as catalyst or solvent in chemical reactions due to their unique chemical and physical properties, such as negligible vapor pressure, adjustable hydrophilic/lipophilic solvating properties, high chemical, and thermal stability, etc. [15-24]. During the last decade, different salts of 1-butyl-3-methylimidazolium [bmim] were used only as a solvent in the Baeyer-Villiger oxidation reaction of aromatic aldehydes. For example, [bmim] PF_6 was applied with hydrogen peroxide/boric acid or m-chloroperbenzoic acid to convert aromatic aldehydes into phenols in less than 4h [18,19]. Bernini et al [17] studied the catalytic activity of hydrogen peroxide/methyltrioxorhenium in [bmim] BF_4 and [bmim] PF_6 on the oxidative conversion of substituted aromatic aldehydes and ketones to the corresponding phenols. They reported that high yields of products in short reaction times and under controlled conditions were obtained by this catalytic system. Recently, some significant research findings have been reported for Lewis and Bronsted acidic ionic liquids as catalyst. However, there isn't any report available where Bronsted acidic ionic liquid has been used as a catalyst in Baeyer-Villiger oxidation of aromatic aldehyde. For this reason, acidic ionic liquids as more environmentally friendly catalysts can be interesting for this reaction.

Aiming to develop the application of SO_3H -functionalized ILs as green catalysts in organic transformations, we described herein a simple, efficient and eco-friendly approach for Baeyer-Villiger oxidation of *para*-anisaldehyde (Scheme 1) with 30% aqueous hydrogen peroxide as oxidant using two acidic ionic liquids based on imidazolium cation BMSIL and IMSIL (Scheme 2) as homogeneous recyclable catalysts.

EXPERIMENTAL SECTION

Chemicals and instruments

All the chemicals (AR grade) were commercially available and used without further purification. Elemental analyses were performed by Leco, CHNS-932. IR spectra were recorded by a Jasco FT/IR-680 plus

spectrophotometer using KBr pellets. NMR spectra in DMSO-d_6 were obtained by using 400 MHz Bruker instrument and TMS as the internal standard. In each experiment, the products were analyzed with Chrompack GC Model CP9001 equipped with Varian capillary column (50 m, 0.25 mm, 0.25 μm) and FID detector. The parameters for the temperature program of GC analysis were: Initial temperature=60 $^\circ\text{C}$ (2min); final temperature=220 $^\circ\text{C}$ (5min), heating rate=15 $^\circ\text{C}/\text{min}$.

Synthesis of the catalysts

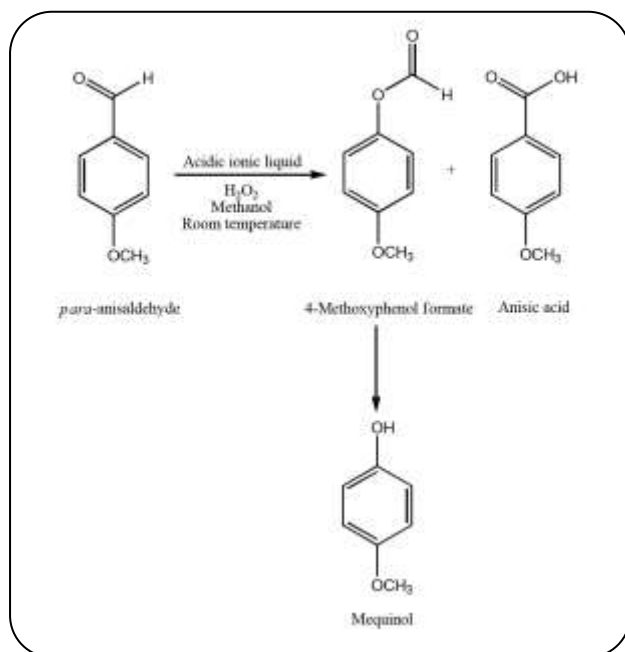
The two acidic ionic liquids used in this work were prepared according to previously reported methods with some modification [25].

Synthesis of 3-dodecyl-1-methyl-1H-imidazolium hydrogen sulfate (IMSIL)

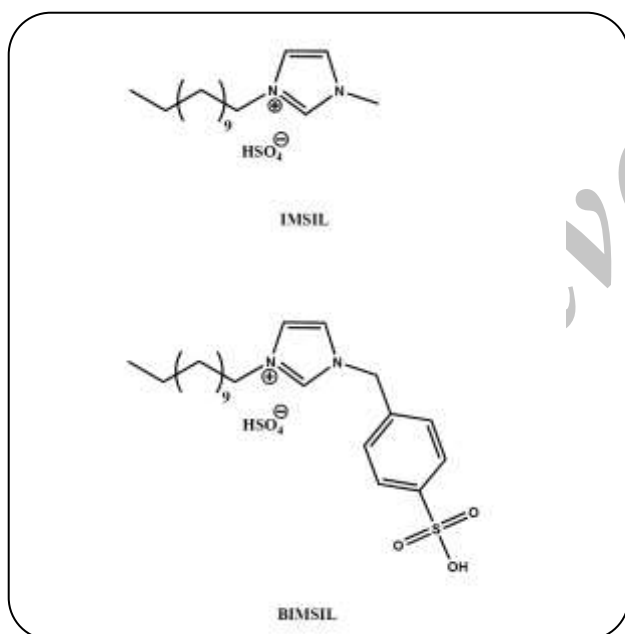
1-methylimidazole (1.24 g, 15 mmol), was dissolved in 60 mL acetonitrile in a three-neck round bottom flask and 3.73 g (15mmol) of 1-bromododecane was added dropwise to the mixture. Then the mixture was refluxed for 72 h. After cooling and filtration, the resulting ionic liquid (IMIL) was recrystallized twice in ethyl acetate (100 mL) and then dried under vacuum at 70 $^\circ\text{C}$ for 12 h. To the 10 g concentrated H_2SO_4 (98 %), that previously cooled in an ice bath, IMIL was added slowly and mixed at this temperature for 8 h. After this time, the mixture was stirred for 24 h at 80 $^\circ\text{C}$ to form IMSIL. Upon completion, the reaction mixture was cooled in an ice bath and then the solid product separated and dried under high vacuum at 70 $^\circ\text{C}$ for 4 h, yielding 5.1 g (97% yields) product. FT-IR (KBr, cm^{-1}): 3454, 3123, 3005, 2919, 2851, 1616, 1559, 1458, 1428, 1376, 1194, 1133, 1015, 763, 702, 623, 569, 454. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.21 (s, 1H, N-CH-N), 7.35-7.26 (m, 2H, Im-H), 4.50 (t, 2H, N-CH₂), 3.88 (s, 3H, CH₃), 1.91 (pent, 2H, N-CH₂-CH₂), 1.21 (m, 18H, CH₂₍₉₎), 0.83 (t, 3H, CH₃). Anal. calcd. For $\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_4\text{S}$ (M.W.=348.50): C, 55.14; H, 9.26; N, 8.04; S, 9.20 found: C, 55.10; H, 9.28; N, 8.18; S, 9.33.

Synthesis of 3-dodecyl-6-sulfo-1-(4-sulfobenzyl)-1H-imidazolium hydrogen sulfate (BIMSIL)

In a three-neck round bottom flask equipped with a condenser, 150 mL THF was stirred at 60 $^\circ\text{C}$ for 20 min with 20.73 g (150 mmol) K_2CO_3 . To this suspension,



Scheme 1: Baeyer-Villiger reaction of anisaldehyde by Brønsted acidic ionic liquids and hydrogen peroxide.



Scheme 2. Synthesized ionic liquids in this work.

6.81 g (100 mmol) of 1H-imidazole was added and then the mixture was refluxed for 2 h. Subsequently, 17.10 g (100 mmol) of benzyl bromide was added dropwise over a period of 45 min, and then the mixture was refluxed for 24 h. The solution was cooled to room temperature and about 40 mL of water was added. The aqueous layer was removed and extracted three times with dichloromethane.

The combined organic layers were added to the THF solution and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum. 1-benzylimidazole (2.37 g, 15 mmol), was dissolved in 60 mL acetonitrile in a three-neck round bottom flask and 3.73 g (15mmol) of 1-bromododecane was added dropwise and the mixture was refluxed for 72 h. After cooling and filtration, the resulting ionic liquid (BIMIL) was recrystallized twice in ethyl acetate (100 mL) and then dried under vacuum at 70 °C for 12 h. To the 10 g concentrated H₂SO₄ (98 %) that previously cooled in an ice bath, BIMIL was added slowly and mixed at this temperature for 8 h. After this time, the mixture was stirred for 24 h at 80 °C to form BIMSIL. Upon completion, the reaction mixture was cooled in an ice bath and then the solid product separated and dried under high vacuum at 70 °C for 4 h (6.8 g, 13.6 mmol, 91% yield). FT-IR (KBr, cm⁻¹): 3455, 3127, 3030, 2923, 2852, 1616, 1562, 1489, 1457, 1428, 1377, 1342, 1223, 1192, 1065, 1012, 852, 765, 702, 618, 585. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.34 (s, 1H, N-CH-N), 7.59-7.30 (m, 6H, Im-H and Ar-H), 5.75 (s, 2H, CH₂), 4.44 (t, 2H, N-CH₂), 1.97 (pent, 2H, N-CH₂-CH₂), 1.20 (m, 18H, CH₂(9)), 0.84 (t, 3H, CH₃). Anal. calcd. For C₂₂H₃₆N₂O₇S₂ (M.W.=504.66): C, 52.36; H, 7.19; N, 5.55; S, 12.71 found: C, 52.28; H, 7.18; N, 5.62; S, 12.48.

The Hammett acidity of Brønsted acidic ionic liquids

For determination of H₀ values of Brønsted acidic ionic liquids, the similar procedure described by Chungu Xia *et al.* [26] was used. Dichloromethane solutions of the ionic liquids (5×10⁻³ mol/L) were prepared from dried dichloromethane and 4-nitroaniline (1.5×10⁻⁴ mol/L) was used as a basic indicator.

General procedure for Bayer-Villiger oxidation

The 1.36 g (10 mmol) of *para*-anisaldehyde, 10 mL of Methanol and ionic liquid (3% based on the mmol of *para*-anisaldehyde) were added to a 25 mL round-bottom flask. Then, 1.3 g hydrogen peroxide (30% aqueous solution) was added, and the reaction mixture stirred and maintained at the room temperature for 3 hours. On completion reaction, Mequinol and anisic acid were identified as major oxidation products by GC-MS analysis.

Additionally, the concentration of H₂O₂ in the reaction mixture was checked by iodometric titration.

Table 1: Effect of different catalysts on the Baeyer–Villiger reaction of anisaldehyde.

Entry	Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)	
				Anisic acid	Mequinol
1	H ₂ SO ₄	25	38	33	67
2	IMSIL	25	35	29	71
3	BIMSIL	25	72	18	82

Reaction conditions: reaction time = 3 h, amount of catalyst = 3 % (based on the mmol of *para*-anisaldehyde).

It is necessary to mention that in the absence of *para*-anisaldehyde the stability of H₂O₂ was tested in the desired reaction conditions and result showed that the concentration of H₂O₂ hadn't changed.

RESULTS AND DISCUSSION

The effect of different catalysts

The Baeyer–Villiger reaction of *para*-anisaldehyde was carried out over various synthesized ionic liquids at 25 °C for 3 h (Table 1). Also, we used H₂SO₄ as an industrial Brønsted acid catalyst for comparison with synthesized catalysts in this work. The result showed that the best conversion was achieved when we used BIMSIL ionic liquid as the catalyst than using the other catalysts.

The mechanism of Baeyer–Villiger reaction *para*-anisaldehyde in the presence of Brønsted acidic ionic liquid can involves four steps: (I) Activation of carbonyl group by the catalyst (II) Nucleophilic addition of hydrogen peroxide to the carbonyl group of substrate to produce Criegee tetrahedral adducts intermediate (III) Intramolecular migration of a substituent from carbon to oxygen with cleavage of the peroxide bond to generate 4-methoxyphenyl formate (IV) Hydrolysis of 4-methoxyphenyl formate to Mequinol by an acid catalyst. It must be pointed out that in most of the Baeyer–Villiger oxidation of aldehydes especially in a protic solvent, the preferred product is the alcohol rather than the ester [20]. Clearly, the catalyst with higher number of Brønsted acidic functions should have more efficiency in this Baeyer–Villiger reaction and hydrolysis of the ester formed in the first oxidation step to phenol. In the present study, the acid strength value (H_0) of acidic ionic liquids were measured by the Hammett method with UV-visible spectroscopy.²⁵ This method consists of calculating the protonation extent of uncharged indicator bases in a solution, in terms of the measurable ratio of $[I]/[IH^+]$ that could be determined from the measured absorbance

differences of 4-nitroaniline ($pK(I)_{aq} = 0.99$) as basic indicator at 349 nm (A_{max}) in dichloromethane solution, before ($[I]$) and after addition of Brønsted acidic ILs ($[IH^+]$). The Hammett acidity function, H_0 , was calculated by using Eq. (1).

$$H_0 = pK(I)_{aq} + \log([I]/[IH^+]) \quad (1)$$

From data presented in Table 2, the acidity of IMSIL ($H_0 = 0.34$) is higher than BIMSIL ($H_0 = 0.87$).

According to the elemental analysis and Hammett acidity function results, the BIMSIL catalyst has more Brønsted acidic functions than IMSIL catalyst. Because of the mentioned facts, the BIMSIL ionic liquid was chosen for further studies.

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The effect of the amount of catalyst

Table 3 shows the results of Baeyer–Villiger reaction *para*-anisaldehyde using a different amount of BIMSIL as a catalyst. The result showed that the production Mequinol improved with an increase in the amount of catalyst to 5 mol.% (based on the mmol of *para*-anisaldehyde), because a higher number of acid sites were accessible with an increase in the quantity of catalyst but a further increase to 7 mol.% did not have more influence on the phenol production [1]. In addition, we carried out control experiment under identical conditions in absence of a catalyst. In this case only traces of product were detected. Consequently, the favoured amount of the catalyst was 5 mol %.

The Effect of reaction time

on the Baeyer–Villiger reaction *para*-anisaldehyde determined by using 5 wt % BIMSIL catalyst and 25 °C,

Table 2: Calculation and comparison of H_0 values of different ionic liquids in CH_2Cl_2 .

Entry	Ionic liquid	A_{max}^a	[I] (%)	[IH ⁺] (%)	H_0
1	Blank	2.28	100	0	-
2	IMSIL	0.99	18.2	81.2	0.34
3	BIMSIL	0.93	43.3	56.6	0.87

$H_0 = pK(I)_{aq} + \log([I]/[IH^+])$, 4-nitroaniline ($pK(I)_{aq} = 0.99$) as basic indicator.

a = The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 349 nm in CH_2Cl_2 .

Table 3: Effect of amount of catalyst on the Baeyer-Villiger reaction of anisaldehyde.

Entry	Catalyst	Amount of catalyst (%)	Conversion (%)	Selectivity (%)	
				Anisic acid	Mequinol
1	BIMSIL	-	5	94	6
2	BIMSIL	1	29	32	68
3	BIMSIL	3	72	18	82
4	BIMSIL	5	95	6	94
5	BIMSIL	7	96	7	93

Reaction conditions: reaction time = 3 h, reaction temperature = 25 °C.

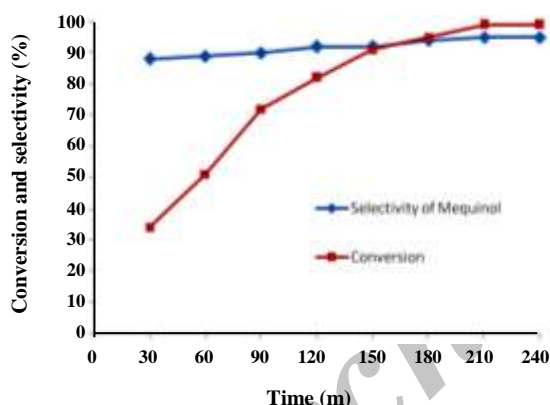


Fig. 1: Effect of reaction time on the Baeyer-Villiger reaction of anisaldehyde.

as reaction conditions (Fig. 1). By increasing the time of the reaction from 30 min to 210 min, the conversion increased from 38 % to 99 %, while the selectivity to Mequinol changed a little. The reaction conversion and Mequinol selectivity almost kept unchanged after 3.5h.

The effect of the substituent in the aromatic ring

Mechanism of the reaction can be tracked by the effect of substituents in the aromatic ring. Table 4 shows the effect of the substituent in the aromatic aldehyde on the Baeyer-Villiger reaction conversion and

selectivity of products. These results demonstrate that the migrating ability of the aromatic group is increased by electron donating substituents and as a consequence, the selectivity of phenol product and reaction conversion should be improved. A similar effect is observed for the phenol selectivity which is shifted from 94% for the methoxy substituent to zero percent for the nitro substituent which yields only the corresponding benzoic acid. As a consequence the electron-donating substituents in *para* position help migration of an aromatic group over the hydrogen migration.

Effect of the solvent

The effect of various solvents on the Baeyer-Villiger oxidation of *para*-anisaldehyde with BIMSIL as a catalyst was also studied. The oxidation reactions were carried out in four solvents with different polarity and the results are given in Table 5. In all of the oxidation reactions, Mequinol was formed as the major product but the highest conversion and selectivity for Mequinol was reached in polar solvent. Clearly, the polarity of the solvent also play an important role on the final catalytic performance when there are two molecules with different polarities including hydrogen peroxide and *para*-anisaldehyde in the reaction media. Based on the mechanism of Baeyer-Villiger oxidation reaction of

Table 4: The effect of the substituent in the aromatic ring.

Entry	Substituent in the aromatic ring	Conversion (%)	Selectivity (%)	
			Corresponding benzoic acid	Corresponding phenol
1	OMe	99	6	94
2	OPh	99	-	100
3	OH	99	4	96
4	Me	90	22	78
5	H	78	88	12
6	NO ₂	69	100	-

Reaction conditions: reaction time = 3.5 h, reaction temperature = 25 °C.

Table 4: Effect of the solvent.

Entry	Solvent	Conversion (%)	Selectivity (%)	
			Anisic acid	Mequinol
1	Dichloromethane	84	27	73
2	1,4- dioxane	89	23	77
3	Acetonitrile	99	8	92
4	Methanol	99	5	95

Reaction conditions: reaction time = 3.5 h, reaction temperature = 25 °C.

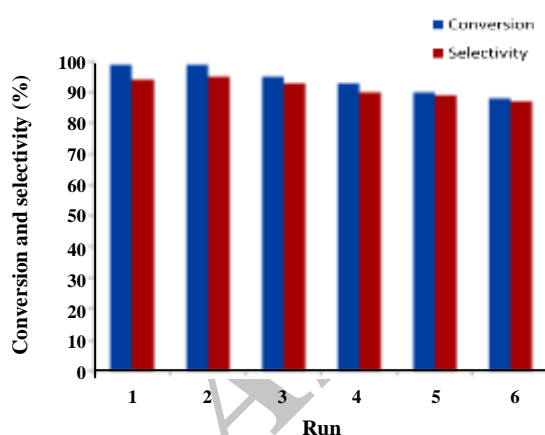


Fig. 2: Catalyst recycling of Baeyer–Villiger reaction of anisaldehyde using BIMSIL.

para-anisaldehyde and miscibility of reaction components with polar solvent at 25 °C. It seems that using polar solvent have some benefits including: (I) hydrogen peroxide can attack faster to the carbonyl group of *para*-anisaldehyde after activation of this group by acidic ionic liquid and (II) protic solvent such as methanol can help to hydrolysis of phenyl format to phenol.

Reusability

The catalytic stability of the BIMSIL as a catalyst in the Baeyer–Villiger oxidation of *para*-anisaldehyde is shown in Fig. 2. By separating the catalyst by centrifugation, washing it with ethyl acetate and drying under vacuum at 70 °C for 4 h, it was used for a new run at the optimum reaction conditions. The activity of the refreshed catalyst after the first cycle remained nearly the same as fresh catalyst, and the decrease after six runs in conversion (88 %) and selectivity (87 %) was satisfactory.

To test if the sulfur is leaching out from the catalyst to the product during the reaction, the reaction mixture was centrifuged after completion reaction and was subjected to elemental analysis. The analysis shows the sulfur was absent in the reaction mixture that might be related to this fact that the Baeyer–Villiger oxidation reaction was carried out at very mild reaction condition in this study.

In summary, different homogeneous catalysts systems such as Hydrogen peroxide/boric acid and *m*-chloroperbenzoic acid were useful reagents to convert aromatic aldehydes to the corresponding phenols, but these procedures required long reactions time, in some

cases up to more than 12 h. According to the literature, the heterogeneous Brønsted or Lewis acids type catalysts, with hydrogen peroxide as an oxidant, are more environmentally friendly and efficient catalysts than homogeneous ones for Baeyer–Villiger oxidation of aldehydes to corresponding phenols [15,17]. Among different heterogeneous systems, the best catalytic system (Sn-zeolite beta/ H_2O_2 / 80 °C/ 7h) with 87% conversion and 95% selectivity of Mequinol was reported by Corma *et al.* [1]. However, in the present study, high conversion (99%) and selectivity (95%) at mild reaction conditions (at room temperature, 3.5 h) makes BMSIL as very attractive and one of the best homogeneous recyclable catalyst in respect of Baeyer–Villiger oxidation of different aldehydes.

CONCLUSIONS

The results showed the good catalytic efficiency for the Baeyer–Villiger oxidation of para-anisaldehyde to Mequinol with hydrogen peroxide over the acidic ionic liquids. The highest conversion and selectivity toward the phenol is obtained with the BMSIL catalyst in polar solvents. The Baeyer–Villiger oxidation procedure could be carried out at mild conditions, and the BMSIL ionic liquid could be reused several times without significant loss of activity. Furthermore, the influence of different substituents in the aromatic ring on the catalytic activity of the BMSIL ionic liquid was studied. The main product for the benzaldehydes with electron withdrawing substituent was benzoic acid derivatives, while the benzaldehydes with electron donating groups were converted to the corresponding phenols in good yields.

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