

# A Simple and Efficient Oxidant Pd(OAc)<sub>2</sub> Catalyzed Selective Oxidation of Alkyl/Benzyl Alcohols in Presence of Air Using Recyclable Room-Temperature Ionic Liquid (RTIL)

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**Abstract:** 1,3,5-Trimethyl pyrazolium tetrafluoroborate room-temperature ionic liquid was prepared and employed for the selective oxidation of alkyl/benzyl alcohols using palladium acetate by stirring at room-temperature in presence of air (oxygen from air). This green procedure gave products in moderate to good yields. Moreover, the synthesized 1,3,5-trimethylpyrazolium tetrafluoroborate ionic liquid could be recycled for at least three runs without the loss of significant activity.

**Keywords:** Room-temperature, ionic liquid, green, recyclable, oxidation, alkyl/benzylalcohols.

## INTRODUCTION

In the past several years, there has been dramatic increase in the synthesis of novel “green” ionic liquids (ILs). Chemical engineers have been developing ILs to replace the conventional volatile organic solvents that contribute to the serious air pollution [1]. Ionic liquids are class of the chemicals that have potential as benign industrial alternatives; these organic salts have vanishing low vapour pressure and are liquid at ambient conditions and do not evaporate or cause air pollution [2]. Substitution of ionic liquids for traditional organic solvents could potentially improve environmental health and industries could save billions of dollars in future environmental mitigation and clean-up [1].

Room-temperature ionic liquids [3] are gaining academic and industrial world wide attention [4] as these can be used to replace the organic solvents in catalysis [5], synthesis [6, 7] and separations [8]. The unique properties of RTILs enable their use as alternative solvents and may speed the introduction of potentially “green” solvents into sustainable industrial processes.

Various ionic liquids such as imidazolium, pyridinium, piperidinium, morpholinium etc. have been reported in the literature which are used as efficient catalysts and solvents in organic synthesis [9-14]. Keeping in view the importance of reported ionic liquids, we have tried to synthesize a new class of ionic liquids i.e. 1,3,5-trimethylpyrazolium tetrafluoroborate ionic liquid and were able to get the 85% yield.

The selective oxidation of alcohols to the corresponding aldehydes or ketones without over oxidation to corresponding carboxylic acids is a fundamental transformation in both laboratory synthesis and industrial production [15],

since these products are important precursors and intermediates for many drugs, vitamins and fragrances [16,17]. Moreover, it is a challenging task for the chemists. In fact, aerobic oxidation of benzylic/primary and secondary aliphatic alcohols have been reported using Pd(OAc)<sub>2</sub>/pyridine/MS3Ab [18]. Even homogeneous transition metal catalyzed aerobic oxidation of alcohols [19] is also known in literature. In addition to these, there are number of known methodologies [20, 21] but they are associated with certain drawbacks such as toxicity, expensive nature and non-recyclability. However, the oxidations [22-25] using ionic liquids are highly efficient as ionic liquids are easily separable, and recyclable what makes the process more economic.

In the context of Green Chemistry, various catalytic systems have been reported for selective oxidation of alcohols [26-37].

In this paper, we report the simple preparation of novel 1,3,5-trimethylpyrazolium tetrafluoroborate (Scheme 1) and its application in selective oxidation of alkyl/benzyl alcohols using palladium acetate in the presence of air (oxygen from air). In this case, novel 1,3,5-trimethylpyrazoliumtetra-fluoroborate is studied as solvent. Moreover, the novel 1,3,5-trimethyl-pyrazoliumtetrafluoroborate is found to be re-cyclable for atleast three runs what makes the process cost-effective.

## RESULTS AND DISCUSSION

To optimize the reaction conditions, benzyl alcohol was selected as a test substrate. The oxidation was carried out under different conditions with respect to different molar ratios of palladium acetate and different amounts of 1,3,5-trimethylpyrazoliumtetrafluoroborate room-temperature ionic liquid. First of all, different molar ratios of palladium acetate (1 to 5 mol% Pd) were chosen for 2 mmol of benzyl alcohol and 1 mL of ionic liquid. Among various molar ratios of palladium acetate, 4.5 mol% gave optimum results at room temperature, which was selected as the reaction temperature. The benzaldehyde was obtained in 72% yield in 47 h by

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stirring at room-temperature in the presence of air (oxygen from air). Further, to reduce the reaction time, the reaction with test substrate was attempted at high temperature (70 °C). The amount of palladium acetate was also increased but again lower selectivity was obtained. Thus, the optimum conditions selected are: benzyl alcohol (2 mmol), palladium acetate (4.5 mol% Pd), 1,3,5-trimethylpyrazoliumtetrafluoroborate (1mL) and stirring at room-temperature in the presence of air (oxygen from air), room temperature as the reaction temperature.

Different types of 1-butyl-3-methylimidazolium ionic liquids were tried for selective oxidation of benzyl alcohols as shown in Table 2. Comparative study for oxidation of alkyl/benzyl alcohols to aldehydes using different 1-butyl-3-methylimidazolium anion ionic liquids was carried out in case of 3-nitrobenzyl alcohol (2 mmol) and palladium acetate (0.02 g, 4.5 mol%) as shown in Table 2. It was found that the reaction mixture of 3-nitrobenzyl alcohol and palladium acetate when stirred for 36 hours using 1-butyl-3-methyl imidazolium chloride (1 mL) in presence of air (oxygen from air), 62% 3-nitrobenzaldehyde was obtained. When the similar reaction was tried with 1-butyl-3-methylimidazolium tetrafluoroborate and stirred for 24 hours at room-temperature in presence of air (oxygen from air), 78% yield was obtained. Using the same optimum conditions, when the reaction was tried with 1-butyl-3-methylimidazolium aluminate and subjected to stirring for 26 hours at room-temperature in presence of air (oxygen from air), 70% 3-nitrobenzaldehyde was obtained. With 1-butyl-3-methylimidazolium hexafluorophosphate, the reaction mixture was stirred for 30 hours at room-temperature in presence of air, 72% product was obtained. On comparison among different types of 1-butyl-3-methylimidazolium ionic liquids, it was found that with 1-butyl-3-methylimidazolium tetrafluoroborate, reaction took less time and gave maximum yield. So for comparison with different ionic liquid, similar reaction was also tried with 1,3,5-trimethylpyrazolium ionic liquids as shown in (entry 5, Table 1). When the reaction mixture of 3-nitrobenzyl alcohol (2 mmol), palladium acetate (0.025 g, 4.5 mol %) and 1,3,5-trimethylpyrazolium chloride (1 mL) was stirred for 32 hours at room-temperature in presence of air (oxygen from air), 68% corresponding aldehyde was obtained. With 1,3,5-trimethylpyrazoliumtetrafluoroborate, reaction mixture was stirred for 18 hours at room-temperature in presence of air (oxygen from air), 3-nitrobenzaldehyde was obtained in 80 % yield. But with 1,3,5-trimethyl pyrazolium aluminate, reaction mixture was stirred for 25 hours at room-temperature in presence of air, 3-nitrobenzaldehyde was obtained in 73 % yield. When the similar reaction was repeated with 1,3,5-trimethylpyrazolium hexafluorophosphate and stirred for 20 hours at room-temperature in presence of air (oxygen from air), corresponding aldehyde was obtained in 78% yield as shown in Table 1. Among different type of 1,3,5-trimethylpyrazolium ionic liquids, reaction with tetrafluoroborate took less time and gave maximum yield. On comparing the similar reaction with different type of ionic liquids such as 1-butyl-3-methyl imidazolium anion and 1,3,5-trimethylpyrazolium anion, it was found that 1,3,5-trimethylpyrazoliumtetrafluoroborate gave maximum 80% yield in 18 hours stirring at room temperature in presence of air (oxygen from air).

**Table 1. Comparative study for Oxidation of Alkyl/Benzyl Alcohols to Aldehydes Using Different Pyrazolium Anion Ionic Liquids at Room Temperature in Presence Of Air (Oxygen from Air)**

Synthesized Ionic Liquid	Time (h)	Yield (%)
1,3,5-trimethylpyrazolium chloride	32	68
1,3,5-trimethylpyrazoliumtetrafluoroborate	18	80
1,3,5-trimethylpyrazolium aluminate	25	73
1,3,5-trimethylpyrazolium hexafluorophosphate	20	78

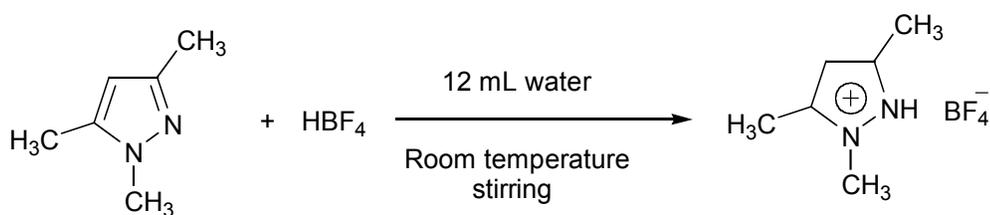
**In case of entry 5, reaction conditions are:** To a mixture of 3-nitrobenzylalcohol (2 mmol) and 1,3,5-trimethylpyrazolium tetrafluoroborate (1 mL) in a round-bottom flask (50 mL), palladium acetate (0.02 g, 4.5 mol%) was added. It was stirred for 18 hours at room-temperature in presence of air (oxygen from air), product was isolated in 80 % yield.

**Table 2. Comparative Study for Oxidation of Alkyl/Benzyl Alcohols to Aldehydes Using Different 1-Butyl-3-Methylimidazolium Anion Ionic Liquids at Room Temperature in Presence of Air (Oxygen from Air)**

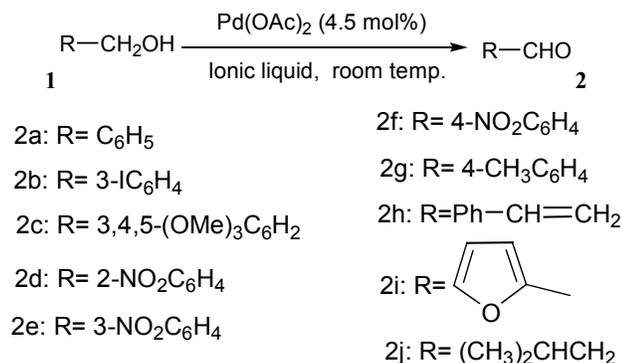
Available Ionic Liquid	Time (h)	Yield (%)
1-butyl-3-methylimidazolium chloride	36	62
1-butyl-3-methylimidazoliumtetrafluoroborate	24	78
1-butyl-3-methylimidazolium aluminate	26	70
1-butyl-3-methylimidazoliumhexafluorophosphate	30	72

**In case of entry 5, reaction conditions are:** To a mixture of 3-nitrobenzylalcohol (2 mmol) and 1-butyl-3-methylimidazoliumtetrafluoroborate (1 mL) in a round-bottom flask (50 mL), palladium acetate (0.02 g, 4.5 mol%) was added. It was stirred for 24 hours at room-temperature in presence of air (oxygen from air), product was isolated in 78 % yield.

To demonstrate the versatility of the developed protocol, benzyl alcohols substituted with various electron-donating and electron-withdrawing groups were selected (Scheme 2) and found that moderate to good results were obtained (Table 3). In case of 3-iodobenzyl alcohol, corresponding aldehyde was obtained in 70 % isolated yield by stirring for 35 hours (entry 2, Table 3) at room-temperature in presence of air (oxygen from air) and rest being the starting material. In case of trimethoxy benzylalcohol, corresponding aldehyde was obtained in 80 % yield by stirring for 25 hours at room-temperature in presence of air (oxygen from air), 20% benzyl alcohol was left behind. After completion of reaction monitored by TLC, ethylacetate was added followed by concentration and then pet.ether or n-hexane was added, ionic liquid got separated as droplets on the surface. Then the product from organic layer was obtained after removal of solvent under reduced pressure. Among electron-withdrawing groups (entries 3, 4 and 5, Table 3), m-nitrobenzyl alcohol gave m-nitrobenzaldehyde in 80 % yield by stirring for 18 hours at room-temperature in presence of air (oxygen from air) in entry 5 and it was also found that some of the starting material was not utilized. Even benzyl alcohol substituted with electron releasing group i.e.4-methyl benzyl alcohol gave significant 75 % yield by stirring for 21 hours (entry 6, Table 3) at room-temperature in presence of air (oxygen from air). This reaction worked well even for oxidation of unsaturated alcohol i.e. cinnamyl alcohol which



Scheme 1.



Scheme 2.

gave cinnamaldehyde in 65% yield (entry 8, Table 3) by stirring at room-temperature in presence of air (oxygen from air). Heterocyclic benzyl alcohols such as furfuryl alcohol also underwent oxidation with high selectivity and furfuraldehyde was obtained in 71% yield. Aliphatic alcohols such as isoamyl alcohol also underwent oxidation in less time than benzyl alcohol (entry 9, Table 3).

Oxidation of alkyl/benzyl alcohols to aldehydes was also reported in literature using different organic solvents. After carrying out the reaction using volatile organic solvents, disposal of organic solvents can enhance environmental pollution. In order to overcome the mentioned disadvantage, we decided to report the oxidation of alkyl/benzyl alcohols in greener room-temperature ionic liquid.

### RECYCLABILITY OF IONIC LIQUID

1,3,5-Trimethylpyrazolium tetrafluoroborate was found to be recyclable for at least 3 runs. The reaction in case of 3-iodobenzyl alcohol was carried out for 3 consecutive runs (1<sup>st</sup> run: 70% after 35 h; 2<sup>nd</sup> run: 68% after 38 h; 3<sup>rd</sup> run: 67% after 42h) with the same ionic liquid.

These results demonstrated that there was no significant loss of activity of ionic liquid as it was recyclable.

### EXPERIMENTAL

#### General

The chemicals used were purchased from Aldrich Chemical Company. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. The <sup>1</sup>H NMR data were recorded on Bruker DPX 200 (200 MHz) spectrometer using TMS as an internal standard. The IR spectrum were recorded on Perkin-Elmer FTIR spectrophotometer using KBr windows and mass spectrum were recorded using Micromass Q-ToF micro.

### Preparation of Novel 1,3,5-Trimethylpyrazoliumtetrafluoroborate Ionic Liquid and its Characterization

To 1 mmol of 1,3,5-trimethylpyrazole and 3 mmole of HBF<sub>4</sub>, 12 mL of distilled water were added. The resulting mixture was stirred at room temperature for 54 h. After completion of the reaction (monitored by TLC), water was distilled off to get the required 1,3,5-trimethylpyrazoliumtetrafluoroborate in 85% yield (Scheme 1).

A series of novel 1,3,5-trimethylpyrazolium ionic liquids are prepared and tested for selective oxidation of benzyl/alkyl alcohols using palladium acetate at room temperature and comparative studies are drawn in Tables 1 and 2. These studies have shown that in terms of reaction time and yield, 1,3,5-trimethyl pyrazolium tetrafluoroborate was superior. Thus, we report the preparation of 1,3,5-trimethylpyrazoliumtetrafluoroborate, its characterization and its application in selective oxidation of benzyl alcohols using palladium acetate at room temperature in presence of air (oxygen from air).

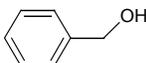
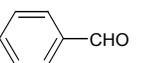
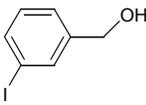
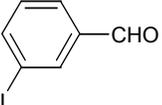
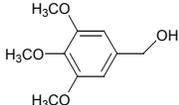
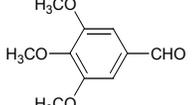
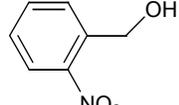
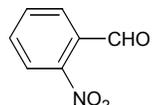
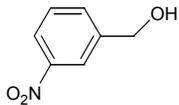
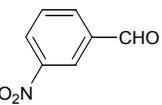
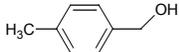
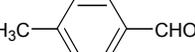
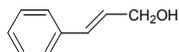
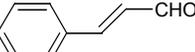
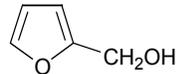
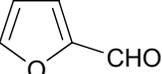
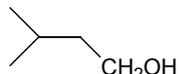
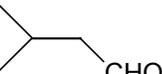
The structure of 1,3,5-trimethylpyrazoliumtetrafluoroborate was confirmed on the basis of IR, <sup>1</sup>H NMR and mass spectral data.

### Characterization of 1,3,5-Trimethylpyrazoliumtetrafluoroborate

The IR spectrum [38] of 1,3,5-trimethylpyrazoliumtetrafluoroborate gave a strong absorption band at 3500 cm<sup>-1</sup> which was attributed to the presence of -NH group and other absorption bands at 2973, 2910, 2075 and 1448 cm<sup>-1</sup> were due to the presence of -CH<sub>3</sub>, -C-H, N-N and bending -CH groups respectively.

The <sup>1</sup>H NMR spectrum [38] of 1,3,5-trimethylpyrazoliumtetrafluoroborate was reported in CDCl<sub>3</sub>. The methyl groups at position C-3 and C-5 were also displayed as singlets at 4.0 δ and 2.25 δ respectively while the methyl proton at C-1 position (N-CH<sub>3</sub>) was observed as a singlet at

**Table 3. Oxidation of Alkyl/Benzyl Alcohols to Corresponding Aldehydes Using Palladium Acetate and 1,3,5-Trimethylpyrazolium Tetrafluoroborate at Room Temperature in Presence of Air (Oxygen from Air)**

Entry	Reactant	Product <sup>a</sup>	Time (h)	Isolated Yield <sup>b</sup> (%)	m.p. or b.p. (lit m.p./b.p.) [39] (°C)
1 <sup>c</sup>			47	72	Liq. (b.p. 178-179)
2 <sup>c</sup>			35	70	55-56 (57-60)
3 <sup>c</sup>			25	80	71-73 (72-74)
4 <sup>c</sup>			28	65	41-42 (42-44)
5 <sup>c</sup>			18	80	54-56 (55-58)
6 <sup>c</sup>			22	70	102-104 (103-106)
7 <sup>c</sup>			21	75	Liq. (b.p. 204-205)
8 <sup>c</sup>			32	65	Liq. (b.p. 250)
9 <sup>c</sup>			35	71	Liq. (b.p. 162)
10 <sup>c</sup>			36	60	Liq. (b.p. 90)

<sup>a</sup>All products were characterized by IR, <sup>1</sup>H NMR, mass spectral data and comparison with authentic samples available commercially or prepared according to the literature reported methods.

<sup>b</sup>Yields refer to the isolated yields.

<sup>c</sup>These products were purified by passing through a column of silica gel and elution with ethylacetate and petroleum ether.

5.25  $\delta$  value. The sharp singlet due to vinylic proton (-CH=C-) was observed at 7.30  $\delta$ . The proton which is attached to nitrogen in 1,3,5-trimethylpyrazolium tetrafluoroborate at position-2 was observed as a broad singlet at 12.25  $\delta$ . The mass spectrum displayed molecular ion peak at 111.1 (m/z) which was due to the presence of 1,3,5-trimethylpyrazolium cation (Fig. 1).

#### General Procedure for Selective Oxidation of Alkyl/Benzyl Alcohols to Aldehydes

To a mixture of alkyl/benzyl alcohol (2 mmol) and 1,3,5-trimethylpyrazolium tetrafluoroborate (1 mL) in a round-bottom flask (50 mL), palladium acetate (0.02 g, 4.5 mol%) was added. The reaction mixture was stirred at room

temperature in the presence of air (oxygen from air) for the appropriate time (Table 3). After completion of the reaction (monitored by TLC), the reaction mixture was dissolved in ethyl acetate (16 mL), concentrated to half and then, pet. ether (4 mL) was added till the ionic liquid got separated. The product was obtained after removal of solvent under reduced pressure and then crystallized either from ethyl acetate or passing through a column of silica gel and elution with ethylacetate and petroleum ether.

The structures of products were confirmed by <sup>1</sup>H NMR, IR and mass spectral data and comparison with authentic samples available commercially or prepared by literature methods.

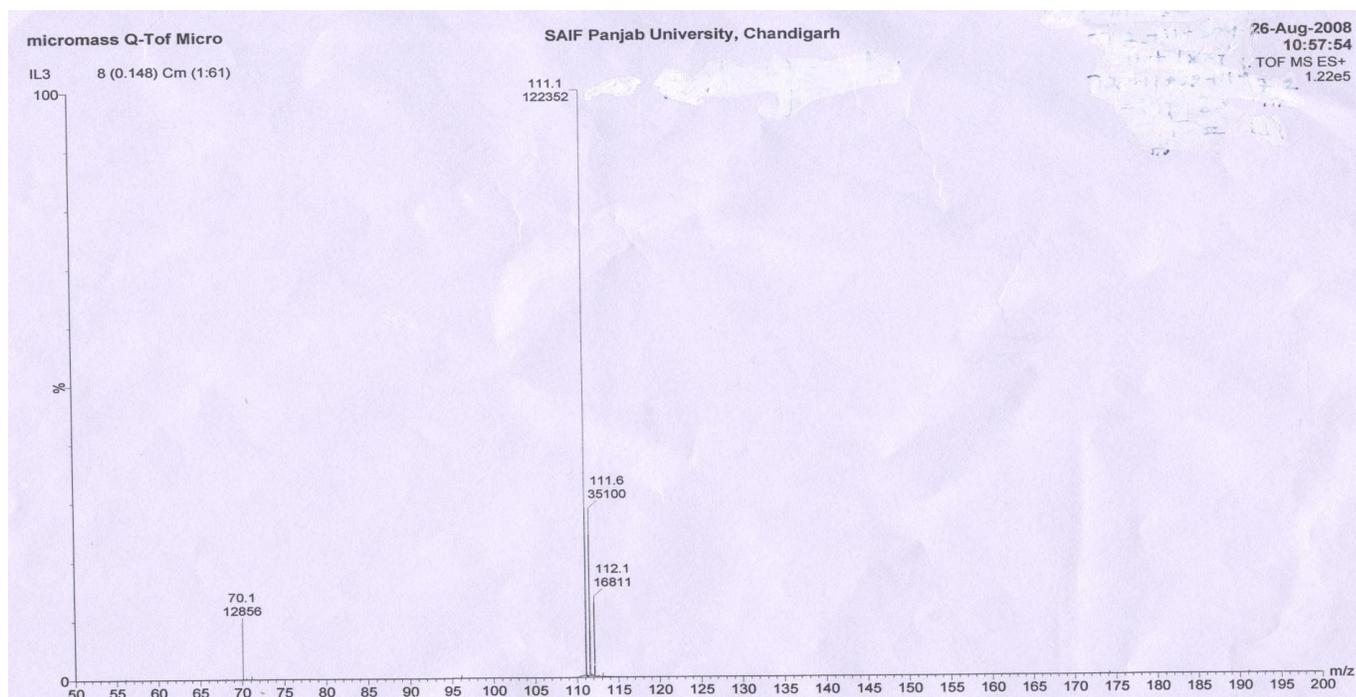


Fig. (1). Mass spectra for ionic liquid.

#### Spectral Data of Synthesized Compounds (Entries 1-10)

**Entry1.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.68-6.71 (d, 2H, Harom), 7.30-7.50 (m, 3H, Harom), 9.05 (s, 1H, CHO); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1695, 3300; **Mass: m/z** ( $\text{M}^+$ ): 106.

**Entry2.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (7.10-7.20 (d, 2H, Harom), 7.73-7.45(m, 1H, Harom), 7.62 (s, 1H, Harom), 9.05 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1695, 3300; **Mass: m/z** ( $\text{M}^+$ ):158.

**Entry3.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  4.01 (s, 9H, 3X - $\text{OCH}_3$ ), 7.05 (s, 2H, Harom), 9.05 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1275, 1690, 3300; **Mass: m/z** ( $\text{M}^+$ ): 196.

**Entry4.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  7.20-7.24 (d, 2H, Harom), 7.35-7.45 (m, 2H, Harom), 9.05 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1440, 1720, 3300; **Mass: m/z** ( $\text{M}^+$ ): 151.

**Entry5.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) : $\delta$  7.36 (s, 1H, Harom), 8.30-8.32(d, 2H, Harom), 8. 70- 8.72 (m, 1H, Harom), 10.00 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1440, 1720, 3300; **Mass: m/z** ( $\text{M}^+$ ): 151.

**Entry6.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.10-8.50 (dd, 4H, Harom), 10.00 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1440, 1720, 3300; **Mass: m/z** ( $\text{M}^+$ ): 151.

**Entry7.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.23 (s, 3H,  $\text{CH}_3$ ), 7.24-7.28 (dd, 4H, Harom), 9.05 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1720, 2800, 3300; **Mass: m/z** ( $\text{M}^+$ ): 120.

**Entry8.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.90 (d, 1H, =CH), 6.82 (d, 1H, CH=), 7.50-7.70 (m, 5H, Harom), 9.05 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1690, 3000, 3300; **Mass: m/z** ( $\text{M}^+$ ): 120.

**Entry 9.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.92-6.94 (d, 2H, Harom), 7.50-7.60 (m, 1H, Harom), 9.07 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1690, 3000, 3300; **Mass: m/z** ( $\text{M}^+$ ): 96.

**Entry 10.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.21-1.23 (d, 1H, CH), 1.35 (dd, 2H,  $\text{CH}_2$ ), 4.12-4.16 (m, 7H, 2X - $\text{CH}_3$ ), 9.07 (s, 1H, Harom); **IR** (**KBr**,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ): 1690, 2800, 2925; **Mass: m/z** ( $\text{M}^+$ ): 86.

#### CONCLUSION

In conclusion, we have reported the simple preparation of novel 1,3,5-trimethylpyrazoliumtetrafluoroborate room-temperature and its application for the selective oxidation of alkyl/ benzyl alcohols using efficient oxidant palladium acetate at room-temperature in the presence of air (oxygen from air). Comparative studies have also been carried out which show that the synthesized ionic liquid is found to be highly efficient and recyclable for selective oxidation of alkyl/ benzyl alcohols. Moreover, the products are obtained in moderate to good yields and are in a state of high purity. The most important advantage of this method over existing ones is that the newly synthesized ionic liquid is recyclable for atleast three runs what makes the process cost-effective. Moreover, work-up procedure is simple and use of greener room-temperature ionic liquid, as these can replace volatile organic solvents, in oxidation falls in the area of "Green Chemistry".

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