



# The oxidation of alcohols in substituted imidazolium ionic liquids using ruthenium catalysts

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It has been demonstrated that ionic liquids based upon substituted imidazolium cations may be used as alternative solvent media for the selective oxidation of alcohols to aldehydes and ketones. The ruthenium catalyst tetrapropylammonium perruthenate has been used in conjunction with either *N*-methylmorpholine-*N'*-oxide or molecular oxygen as oxidants in two different catalytic systems. Benzylic alcohols are oxidized in good to excellent yields whereas aliphatic alcohols require far greater reaction times and give poor yields. The reaction products can be easily removed from the reaction mixture by extraction with diethyl ether.

## Introduction

Ionic liquids are defined as compounds that are comprised entirely of ions and are liquids below 100 °C.<sup>1</sup> They exhibit a number of notable physical properties that may be exploited in synthetic processes. For instance, ionic liquids have negligible vapour pressures, allowing them to be used in high vacuum systems where distillation and/or sublimation techniques are employed to separate reaction products from the reaction mixture. The fact that ionic liquids do not evaporate lies at the heart of their claim to environmental benefit; with ionic liquids many of the containment issues surrounding the use of conventional organic solvents are circumvented.

Ionic liquids are good solvents for other salts and immiscible with many organic solvents. Thus organic reaction products can be easily extracted from ionic liquids containing charged catalysts or biphasic catalysis performed using them. The

synthetic utility of ionic liquids has been reflected in the rapidly increasing volume of literature available. Reaction types successfully performed in ionic liquids include Diels–Alder,<sup>2</sup> Friedel–Crafts,<sup>3</sup> olefin hydrogenation,<sup>4</sup> hydroformylation,<sup>5,6</sup> oligomerization,<sup>7</sup> and Heck and Suzuki coupling reactions.<sup>8,9</sup>

The oxidation of primary alcohols to their aldehydes or carboxylic acids, and secondary alcohols to ketones are fundamental synthetic transformations. However, many oxidation processes rely upon environmentally damaging oxidants and have poor atom efficiencies. Thus, there is an increasing demand for oxidation processes that are catalytic and use environmentally benign oxidants, such as molecular oxygen and hydrogen peroxide.<sup>10,11</sup> It was therefore decided to pursue a line of research which would attempt to utilise such oxidants.

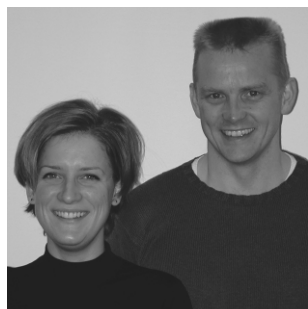
To date few oxidation processes have been performed in ionic liquids. Rhenium and manganese complexes have been used to epoxidize alkenes,<sup>12,13</sup> and nickel acetate to oxidize aromatic aldehydes.<sup>14</sup>

Tetrapropylammonium perruthenate ( $\{[{}^n\text{Pr}_4\text{N}][\text{RuO}_4]\}$ , 'TPAP') in conjunction with *N*-methylmorpholine-*N'*-oxide as a co-oxidant, acts as a mild and selective catalyst for the oxidation of alcohols to aldehydes and ketones.<sup>15,16</sup> Reactions proceed rapidly with high turnover numbers, when performed in organic solvents and the presence of powdered molecular sieves.<sup>17</sup> TPAP is now commonly used in laboratory procedures and methods by which this catalyst may be supported and subsequently recycled have been developed.<sup>18</sup> TPAP was chosen as catalyst because it is well characterized, and comprises of an inorganic anion and large organic cation. It was expected that the catalyst would be immobilized in the ionic

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Tom Welton is a Senior Lecturer at Imperial College London. Having first arrived there in 1993 as the Lloyds of London Tercentenary Fellow he became a Lecturer two years later. Although he also has interests in other areas, Tom has worked

with ionic liquids since his Ph. D. studies at the University of Sussex. Tom's group focus on understanding how the environment in which a reaction is occurring changes the observed reactivity. They study both stoichiometric and catalytic reactions and refer their results to detailed measurements of interactions between reacting species and their environments.



## Green Context

Ionic liquids have attracted great attention as potentially green solvents for many organic reactions. Here, they are evaluated for oxidation reactions of alcohols, an area where progress must be made towards clean and selective oxidations. Perruthenate is used in conjunction with *N*-oxide as the oxidant. Alternatively, oxygen can be used, but Cu(I) and a diamine ligand must also be added. Conversions and yields are good and selectivities can also be very high. **DJM**

liquid and that organic substrates would be easily removed by conventional extraction techniques.

## Results and discussion

It was observed that reaction yields were on occasion variable. Two aspects of the catalytic system were identified that could give rise to such variations: (i) the quality of the TPAP and (ii) the quality of the ionic liquid.

Although TPAP is at its most active when absolutely fresh, and activity is lost almost immediately, we have shown that there is minimal further loss between one and six days after synthesis, if stored at low temperatures (Table 1). Further to this, UV analysis of TPAP showed little change in either  $\lambda_{\text{max}}$  or extinction coefficient, even after one month. TPAP was therefore regularly synthesized and stored under  $\text{N}_2$  at  $-18^\circ\text{C}$ .

We found that reactions performed in the same batch of ionic liquid gave consistent results. However, different yields of oxidation product have been obtained when using the same reaction conditions but a different batch of ionic liquid. These differences depend upon (i) the method used to prepare the ionic liquid and (ii) the batch of ionic liquid. Employing the following protocols for the synthesis of an ionic liquid has significantly

reduced much of the variance observed in preliminary studies.

## Preparation of ionic liquid

Good quality 1-butyl-3-methylimidazolium ( $[\text{bmim}]^+$ ) based ionic liquids with the common anions;  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{CF}_3\text{SO}_3]^-$ ,  $[\text{CF}_3\text{CO}_2]^-$  and  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , are *always* free flowing, *colourless* liquids. Conversely, impure ionic liquids are frequently orange–yellow with variable viscosities. The source of the colouration is unknown, however, it has been observed that excessive heating during the synthesis of the imidazolium salt will cause increased colouring of the  $[\text{bmim}]\text{Cl}$ ; colourless ionic liquids cannot be prepared from coloured  $[\text{bmim}]\text{Cl}$ . The colour is removed by multiple recrystallisations (see Experimental section). It should be noted that even a colourless ionic liquid is not necessarily pure.<sup>19</sup>

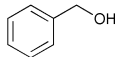
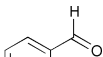
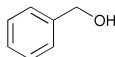
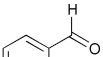
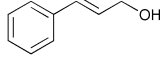
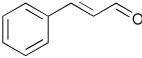
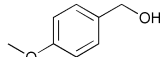
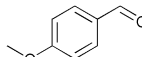

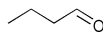
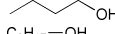
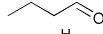
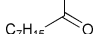
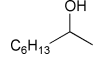
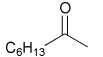
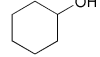
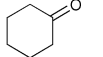
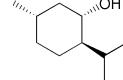
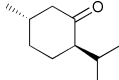
Depending upon the synthetic route used, either halide ions or acid may remain in the ionic liquid, which can have dramatic effects upon catalytic reactions later performed in them. To remove these impurities it is necessary to dissolve the ionic liquid in dichloromethane ('DCM') and wash this solution with water until the washings are halide free (determined by silver nitrate test) or pH neutral. After a final washing, the DCM is then removed *in vacuo*. It has been found that even when using these protocols the acid may still remain, *e.g.*  $[\text{bmim}][\text{CF}_3\text{SO}_3]$ , or be further generated *in situ*, as in the case of  $[\text{bmim}][\text{PF}_6]$ . It has been observed that the most significant fluctuations in the results arise from using ionic liquids prepared by the acid route. Thus, as halide salts have proved simpler to remove, the salt metathesis route has become our method of choice (compare entries 1 and 1a in Table 2).

Even with all due diligence the resultant ionic liquid is still frequently coloured. At this point any residual colour may be removed by passing the liquid through a short pad of acidic

**Table 1** Variation of reaction conditions for the oxidation of benzyl alcohol to benzaldehyde with NMO

Comment	% Conversion
1 g of powdered 4 Å molecular sieves added	70
No molecular sieves added	70
1 equiv. of water added	71
TPAP (1 day old)	70
TPAP (6 days old)	68

**Table 2** Oxidation of alcohols to aldehydes and ketones using TPAP and NMO stirring in  $[\text{bmim}][\text{BF}_4]$  at room temperature with NMO

Entry	Alcohol	Product	% Conversion (2 h) <sup>a</sup>	% Conversion (24 h)	% Lit. value (t/h) <sup>17</sup>
1			70	89	80 (2)
1a <sup>b</sup>			59	—	80 (2)
2			59	97	91 (3)
3			71	95	68 (12)
4			24	—	95 (1)
4a <sup>c</sup>			43	—	—
5	$\text{C}_8\text{H}_{17}\text{OH}$		35	43	—
6			48	56	—
7			48	46 (16 h)	100 <sup>d</sup>
8			62	77	85 (1)

<sup>a</sup> General reaction conditions: TPAP (5 mol%) and NMO (3 mmol) predissolved in  $[\text{bmim}][\text{BF}_4]$  (2 cm<sup>3</sup>), alcohol (2 mmol), 1 atm  $\text{N}_2$ , 2 h stirring at room temperature. <sup>b</sup>  $[\text{bmim}][\text{BF}_4]$  made *via* acid neutralization method. <sup>c</sup> Reaction sonicated for 1 h. <sup>d</sup> Reaction performed by author in DCM.

alumina ( $l = 10$  mm) before use. In extreme cases it is sometimes necessary to stir the ionic liquid with activated charcoal for *ca.* 24 h before passing it through an alumina pad. It is then necessary to thoroughly dry the ionic liquid to the moisture level required, in this case by heating *in vacuo* at 70 °C for 24 h.

### TPAP catalysed oxidations with NMO as co-oxidant

Investigations were initially conducted in the ionic liquid [bmim][BF<sub>4</sub>]. This ionic liquid was chosen because it is stable to air and moisture, as well as being simple and inexpensive to prepare.<sup>20</sup> Control reactions were performed to verify that the ionic liquid was a benign participant in the process and did not itself oxidize the substrate, or in any other way react with it. Preliminary studies showed that unlike in molecular solvents, the addition of powdered molecular sieves did not enhance reaction yields or rates (Table 1).<sup>17</sup> Even the addition of one equivalent of water did not retard reaction rates nor was over-oxidation of the alcohol to the acid observed, unlike perruthenate in aqueous base.<sup>17</sup> Since [bmim][BF<sub>4</sub>] mixes with water in all compositions this cannot be due to the lack of water in the solution. In a recent paper,<sup>21</sup> we have shown that the water in this ionic liquid is principally associated with the anions. Since perruthenate is an anionic species and one would expect it to be surrounded by cations, it may simply never come into contact with water at these levels in the ionic liquid.

Using the TPAP/NMO/[bmim][BF<sub>4</sub>] system it was found that the oxidation of benzylic and allylic hydroxyl groups proceeded smoothly to give good yields within 2 h. In the case of entry 2 of Table 2 no double bond cleavage was observed and no other product of reaction detected, unlike perruthenate in aqueous base.<sup>22</sup> Reaction went to near completion for entries 2 and 3 in 24 h (Table 2). These results show that catalyst is still active even after extended reaction times. With the exception of entry 3 reaction rates are slower in [bmim][BF<sub>4</sub>] than DCM (Table 2), it is possible that this result may simply be due to viscosity effects, [bmim][BF<sub>4</sub>] and DCM have viscosities of 233 cP<sup>23</sup> and 0.4136 cP<sup>24</sup>, respectively. Unactivated primary alcohols reacted sluggishly to give poor yields of aldehyde (entries 4 and 5, Table 2) and unreacted starting material. Unlike the benzylic alcohols, the aliphatic alcohols used for this investigation were immiscible with [bmim][BF<sub>4</sub>]. Hence mass transport in these biphasic systems may have contributed to the low conversions seen. Indeed, it was found that for the oxidation of butan-1-ol to butyraldehyde, the yield could be boosted from 24% in 2 h to 43% in 1 h by sonicating (bath) the reaction mixture (entry 4a, Table 2) to increase the degree of mixing. The secondary alcohols cyclohexanol and menthol were also found to be immiscible with [bmim][BF<sub>4</sub>], slow to oxidize, and gave moderate to fair final yields. Marked differences for the reaction between primary and secondary alcohols are not apparent, and as such it is not possible to determine whether the catalyst is sterically demanding, although it is often suggested that TPAP oxidations occur *via* ruthenate esters.<sup>16</sup>

### TPAP catalysed oxidation using molecular oxygen as oxidant

A closely related system, which was first reported by Osborn and coworkers,<sup>25</sup> was also employed that uses molecular oxygen as oxidant and TPAP as catalyst, in conjunction with CuCl and/or 2-aminopyridine as co-catalysts. TPAP and molecular oxygen when used together were found to oxidize benzyl alcohol to benzaldehyde (as has already been demonstrated in conventional solvents),<sup>26</sup> however the yield of aldehyde obtained in 85 h was poor. In the same period of time no oxidation occurred using only molecular oxygen in the

absence of the perruthenate catalyst. Conversions to the aldehyde were greatest when TPAP and molecular oxygen were used with CuCl, or 2-aminopyridine and CuCl (Tables 3 and 4).

Reactions were performed in the ionic liquid repeating Osborn's conditions (Table 4). Conversions were of a similar degree, so in order to determine the scope of the system further experiments were conducted that varied (i) the catalyst loading, (ii) the reaction temperature and (iii) reaction times. It was found that for benzylic alcohols good yields were obtained when operating at 60 °C and 5 mol% catalyst loading. Other studies showed that the most efficient rates of oxidation occurred when the oxygen was bubbled through the reaction mixture, rather than using air or oxygen blankets.<sup>27</sup> This result is in agreement with the finding that oxygen solubility in ionic liquids is low.<sup>28</sup>

**Table 3** Oxidation of 4-trifluoromethylbenzyl alcohol to 4-trifluoromethylbenzaldehyde in [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] stirring at 60 °C

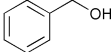
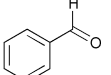
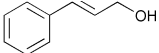
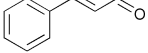
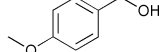
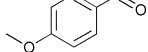
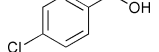
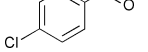
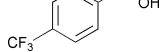
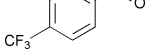
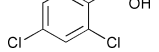
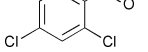






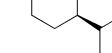
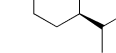
Reaction conditions	% Conversion
TPAP/O <sub>2</sub>	34
TPAP/O <sub>2</sub> /CuCl	> 95
TPAP/O <sub>2</sub> /2-aminopyridine	5
TPAP/O <sub>2</sub> /CuCl/2-aminopyridine	40

### TPAP/O<sub>2</sub>/CuCl/2-aminopyridine system

Unlike the TPAP/NMO system the TPAP/O<sub>2</sub>/CuCl/2-aminopyridine system is almost entirely selective towards benzylic alcohols. As with the NMO system, the alcohols in entries 2 and 3 are smoothly oxidized to the aldehyde in 24 h with no other products being observed (Table 4). The oxidation of benzyl alcohol does not go to completion and whilst benzyl alcohol remains at the end of the reaction a small amount of the condensation product of benzaldehyde and benzyl alcohol, benzoic acid benzyl ester, was also detected. Increasing the electronegativity of the substituent at the *para* position on the benzyl ring impeded reaction rates (compare entries 3–5). Within a 24 h period negligible oxidation of aliphatic alcohols and secondary alcohols is observed (*ca.* 3%, entries 7–10, Table 4) with a maximum conversion of 24% being observed for cyclohexanol in 40 h.

The presence of 1-butyl-3-methylimidazolidone and 1-butyl-3-methylimidazolidine-2,4,5-trione was observed by GCMS in the ether extracts for the oxidation of benzyl alcohol using the TPAP/O<sub>2</sub>/CuCl/2-aminopyridine system. These compounds were not found before the oxidation process, hence oxidation of the ionic liquid is occurring. By deliberately trying to oxidize the ionic liquid in the absence of substrate it was still possible to detect them, but all attempts to isolate and quantify the amount of these compounds formed failed. However, if deprotonation at C2 of the imidazolium ring occurs in the reaction conditions then it is known that in the presence of O<sub>2</sub> and Cu(II), which is almost certainly present in our system, the azolone forms.<sup>29</sup> Although the mechanism for the formation of 1-butyl-3-methylimidazolidine-2,4,5-trione has not been investigated, the formation of the azolone leads to dearomatization of the ring and makes the double bond available for oxidation. Since this is a route to the decomposition of our solvent, we sought to prevent the formation of the azolone. Hence, reactions were performed using 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonimide ([bmmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]) to determine the affect of blocking the C2 position. The conversions were analogous to those observed for [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] and no apparent oxidation of the ionic liquid was detected.

**Table 4** Oxidation of alcohols to aldehydes and ketones using TPAP/O<sub>2</sub>/CuCl/2-aminopyridine and TPAP/O<sub>2</sub>/CuCl systems in different solvents

Entry	Substrate	Product	% Conversion in different solvents (24 h)					
			DCM <sup>a</sup>	[bmim] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>b</sup>	[bmim] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>c</sup>	[bmim] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>d</sup>	[bmim] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>e</sup>	[bmim] [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>f</sup>
1			61 (21 h)	79	91	7	83	92
2			47 (29 h)	31	99	23	99	99
3			52 (23 h)	49	96	30	99	99
4			40 (26 h)	—	91	25	99	—
5			41 (26 h)	—	40	7	99	—
6			51 (25 h)	36	95	21	86	—
7			—	—	5 (40)	2	43	3
8			—	—	10 (40)	6	56	5
9			6 (39 h)	—	24 (40)	6	18	3
10			1 (72 h)	—	2 (40)	1 <sup>g</sup>	6 <sup>g</sup>	1

<sup>a</sup> Literature values, general reaction conditions: [<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>] (1 mol%), CuCl (1 mol%), 2-aminopyridine (5 mol%), 0.5 g of powdered molecular sieves, 1 atm molecular oxygen at 25 °C.<sup>25</sup> <sup>b</sup> [<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>] (1 mol%), CuCl (1 mol%), 2-aminopyridine (5 mol%), 1 atm molecular oxygen at 25 °C. <sup>c</sup> [<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>] (5 mol%), CuCl (5 mol%), 2-aminopyridine (25 mol%), 1 atm molecular oxygen at 25 °C. <sup>d</sup> [<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>] (1 mol%), CuCl (1 mol%), 1 atm molecular oxygen at 25 °C. <sup>e</sup> [<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>] (5 mol%), CuCl (5 mol%), 1 atm molecular oxygen at 60 °C. <sup>f</sup> [<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>] (5 mol%), CuCl (5 mol%), 2-aminopyridine (25 mol%), 1 atm molecular oxygen at 25 °C. <sup>g</sup> Menthol sublimed out of reaction mixture.

### TPAP/O<sub>2</sub>/CuCl system

It can be seen that for benzylic alcohols the conversions are comparable to those of the TPAP/O<sub>2</sub>/CuCl/2-aminopyridine system (entries 1–5, Table 4). However, improved conversions are observed for aliphatic alcohols (entries 7 and 8, Table 4). This may be due to a change in the active catalyst or the solubility of the alcohols being altered. However, this system is clearly superior to the TPAP/O<sub>2</sub>/CuCl/2-aminopyridine one as it does not require 2-aminopyridine.

### Conclusion

In summary, it has been demonstrated that ionic liquids may be used as solvents for the oxidation of alcohols to aldehydes and ketones using TPAP as the source of metal catalyst. TPAP may be used in conjunction with CuCl and O<sub>2</sub> to quantitatively oxidize benzylic alcohols to their aldehydes. The reaction product can be easily extracted from the reaction mixture using diethyl ether.

### Experimental

Reagents were purchased from Avocado Research Chemicals Ltd, Lancaster Synthesis Ltd and Aldrich. RuCl<sub>3</sub>·*n*H<sub>2</sub>O was supplied by Johnson Matthey. Solvents were freshly distilled

and dried by standard procedures (toluene over Na/benzophenone ketyl, MeCN and ethyl acetate over CaH<sub>2</sub>, 1-chlorobutane over P<sub>2</sub>O<sub>5</sub>, and 1-methylimidazole and 1,2-dimethylimidazole from KOH). All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a dry box, unless specified otherwise. <sup>1</sup>H NMR spectra were recorded on a JEOL GSX-270 Fourier-transform NMR. NMR spectra were uncorrected for bulk magnetic susceptibility of the liquid. The mass spectrometry laboratories of the Department of Chemistry recorded GC-MS and FAB spectra. UV–VIS-spectrometry spectra were recorded using a Perkin Elmer Lambda 2 UV-VIS-Spectrophotometer. The spectra were run with the pure solvent in a matched reference cell. For analytical GC an Agilent 4890D Gas Chromatograph equipped with a flame ionisation detector (FID) and an HP-5 crossed linked 5% phenylmethyl siloxane column of length 10 m, diameter 0.53 mm and 1.5 µm film thickness, was used.

#### Preparation of 1-butyl-3-methylimidazolium chloride ([bmim]Cl)

Toluene (50 cm<sup>3</sup>) was transferred *via* syringe to a three neck round bottom flask (500 cm<sup>3</sup>) equipped with a reflux condenser and a magnetic stirrer. 1-Methylimidazole (100 cm<sup>3</sup>, 1.25 mol, 1 equiv.) and 1-chlorobutane (143 cm<sup>3</sup>, 1.37 mol, 1.1 equiv.) were added *via* cannula. The mixture was heated under a N<sub>2</sub> atmosphere at gentle reflux for 24 h. The mixture separated into

two layers when cooled to room temperature, the top layer being toluene and the bottom layer an oil (the product). The flask was then placed in a freezer at  $-18^{\circ}\text{C}$  overnight, whence a white solid formed. The toluene was decanted under a stream of  $\text{N}_2$ . The white solid was recrystallized from the minimum amount of acetonitrile (*ca.*  $75\text{ cm}^3$ ). Aliquots of ethyl acetate were used to wash the salt and the resulting white precipitate was isolated by filtration using standard Schlenk techniques. The salt was then recrystallized in the same manner a second time. The product was dried *in vacuo* for 24 h to give the title compound as a white solid 203 g (1.16 mol, 93 %).  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  (270 MHz,  $\text{CDCl}_3$ ); 0.89 (3H, t,  $J$  7.3 Hz,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.30 (2H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.82 (2H, p,  $J$  7.5 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.05 (3H, s,  $\text{NCH}_3$ ), 4.26 (2H, t,  $J$  7.3 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.40 (1H, m, C(5)H), 7.55 (1H, m, C(4)H), 10.54 (1H, s, C(2)H).<sup>30</sup>  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta_{\text{C}}$  (270 MHz,  $\text{CDCl}_3$ ); 13.49 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 19.51 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 32.21 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 36.60 ( $\text{NCH}_3$ ), 49.82 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 121.94, 123.63 (C(5)H, C(4)H), 138.03 (C(2)H).  $m/z$  (FAB<sup>+</sup>); 83 ( $[\text{C}_4\text{H}_7\text{N}_2]^+$ , 9%), 96 ( $[\text{C}_5\text{H}_8\text{N}_2]^+$ , 3%), 109 ( $[\text{C}_6\text{H}_9\text{N}_2]^+$ , 3%), 139 ( $[\text{bmim}]^+$ , 100%), 313 ( $[\text{bmim}]_2\text{Cl}^+$ , 17%).<sup>31</sup>  $m/z$  (FAB<sup>-</sup>); 35 ( $\text{Cl}^-$ , 47%), 209 ( $[\text{bmim}]_2\text{Cl}_2^-$ , 100%), 383 ( $[\text{bmim}]_2\text{Cl}_3^-$ , 40%).

#### Preparation of 1-butyl-2,3-dimethylimidazolium chloride ([bmmim]Cl)

The same procedure was used as for [bmim]Cl. From 100  $\text{cm}^3$  (1.13 mol, 1 equiv.) of 1,2-dimethylimidazole and 130  $\text{cm}^3$  (1.24 mol, 1.1 equiv.) of 1-chlorobutane there was obtained the title compound as a white crystalline solid 199 g (1.05 mol, 93 %).  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  (270 MHz,  $\text{CDCl}_3$ ); 0.89 (3H, t,  $J$  7.3 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.31 (2H, h,  $J$  7.4 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.74 (2H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.75 (3H, s,  $\text{NCCH}_3\text{N}$ ), 3.98 (3H, s,  $\text{NCH}_3$ ), 4.16 (2H, t,  $J$  7.4 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.49 (1H, d,  $J$  1.98 Hz, C(5)H), 7.77 (1H, d,  $J$  2.0 Hz, C(4)H).  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta_{\text{C}}$  (270 MHz,  $\text{CDCl}_3$ ); 10.50 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13.51 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 19.55 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 31.83 ( $\text{NCH}_3$ ), 35.92 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 48.65 ( $\text{NCCH}_3\text{N}$ ), 121.32, 123.25 (C(5)H, C(4)H), 143.51 (C(2)H).  $m/z$  (FAB<sup>+</sup>); 153 ( $[\text{bmmim}]^+$ , 100%), 123 ( $[\text{C}_7\text{H}_{11}\text{N}_2]^+$ , 3%), 110 ( $[\text{C}_6\text{H}_{10}\text{N}_2]^+$ , 3%), 97 ( $[\text{C}_5\text{H}_9\text{N}_2]^+$ , 10%).

#### Preparation of 1-butyl-3-methylimidazolium trifluoromethanesulfonimide ([bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N])

In a glove box [bmim]Cl (77.5 g, 0.44 mol, 1 equiv.) and  $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$  (132.1 g, 0.46 mol, 1.04 equiv.) were weighed into two three neck, round bottom flasks. At the bench the [bmim]Cl was dissolved in the minimum amount of water (*ca.*  $35\text{ cm}^3$ ) and to this rapidly stirring solution  $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$  was added (as this compound is very hygroscopic it was necessary to add it rapidly). A minimum amount of water was necessary to transfer residual salt into the reaction flask. DCM (*ca.*  $80\text{ cm}^3$ ) was added and the reaction mixture stirred at room temperature for 24 h. The DCM layer containing the product was washed with water until chloride free, as determined by silver nitrate test. The water washings were subsequently extracted with DCM ( $3 \times 50\text{ cm}^3$ ) and the DCM layers recombined. The DCM was removed *in vacuo* and the product passed through a short pad of acidic alumina ( $l = 10\text{ mm}$ ). The final liquid was dried *in vacuo* at  $70^{\circ}\text{C}$  for 24 h to give the title compound as a colourless liquid, 174 g (0.42 mol, 94%).  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  (270 MHz,  $\text{CDCl}_3$ ); 0.93 (3H, t,  $J$  7.2 Hz,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.34 (2H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.82

(2H, p,  $J$  7.6 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.92 (3H, s,  $\text{NCH}_3$ ), 4.14 (2H, t,  $J$  7.4 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.29 (2H, m, C(5)H, C(4)H), 8.70 (1H, s, C(2)H).<sup>30</sup>  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  (270 MHz,  $\text{CD}_3\text{COCD}_3$ ,  $\delta/\text{ppm}$  relative to TMS),  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta_{\text{C}}$  (270 MHz,  $\text{CD}_3\text{COCD}_3$ ,  $\delta/\text{ppm}$  relative to TMS); 12.27 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 18.76 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 31.41 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 35.37 ( $\text{NCH}_3$ ), 49.25 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 119.69 (2C, q,  $^1J_{\text{CF}}$  322 Hz,  $\text{CF}_3\text{SO}_2$ ), 122.04, 123.29 (C(5)H, C(4)H), 135.83 (C(2)H).  $m/z$  (FAB<sup>+</sup>); 83 ( $[\text{C}_4\text{H}_7\text{N}_2]^+$ , 9%), 96 ( $[\text{C}_5\text{H}_8\text{N}_2]^+$ , 3%), 109 ( $[\text{C}_6\text{H}_9\text{N}_2]^+$ , 3%), 139 ( $[\text{bmim}]^+$ , 100%), 558 ( $[\text{bmim}]_2[(\text{CF}_3\text{SO}_2)_2\text{N}]^+$ , 1%).<sup>31</sup>  $m/z$  (FAB<sup>-</sup>); 147 ( $[\text{CF}_3\text{SO}_2\text{N}]^-$ , 5%), 280 ( $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , 100%). IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ ; 3157 (aromatic C–H str., s), 3122 (aromatic C–H str., s), 2967 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H str. asym., s), 2941 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H str. asym., m), 2880 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H str. sym., m), 1572 (aromatic C–C str., m), 1466 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H def., asym., m), 1351 (S–O str., s), 1190 (F–C–F str., s), 1138 (C–F str., s), 843 (aromatic C–H out of plane def., w).<sup>32–34</sup>

#### Preparation of 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonimide ([bmmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N])

The same procedure was used as for [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]. Solvent volumes were scaled as necessary. From 33.16 g (0.176 mol, 1 equiv.) of [bmmim]Cl and 50.46 g (0.176 mol, 1 equiv.) of  $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$  was obtained the title compound as a colourless liquid (61 g, 0.14 mol, 80%).  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  (270 MHz,  $\text{CDCl}_3$ ); 0.93 (3H, t,  $J$  7.4 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.35 (2H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.75 (2H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.57 (3H, s,  $\text{NCCH}_3\text{N}$ ), 3.77 (3H, s,  $\text{NCH}_3$ ), 4.02 (2H, t,  $J$  7.4 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.15 (1H, d, C(5)H), 7.18 (1H, d, C(4)H).  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta_{\text{C}}$  (270 MHz,  $\text{CD}_3\text{COCD}_3$ ,  $\delta/\text{ppm}$  relative to TMS); 8.44 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 12.49 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 18.82 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 31.10 ( $\text{NCH}_3$ ), 34.23 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 47.88 ( $\text{NCCH}_3\text{N}$ ), 119.59 (2C, q,  $^1J_{\text{CF}}$  321 Hz,  $\text{CF}_3\text{SO}_2$ ), 120.49, 122.02 (C(5)H, C(4)H), 143.97 (C(2)H).  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta_{\text{C}}$  (270 MHz,  $\text{CDCl}_3$ ); 9.60 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 13.37 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 19.55 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 31.49 ( $\text{NCH}_3$ ), 35.35 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 48.66 ( $\text{NCCH}_3\text{N}$ ), 120.88, 122.58 (C(5)H, C(4)H), 143.82 (C(2)H).  $m/z$  (FAB<sup>+</sup>); 97 ( $[\text{C}_5\text{H}_9\text{N}_2]^+$ , 7%), 110 ( $[\text{C}_6\text{H}_{10}\text{N}_2]^+$ , 5%), 123 ( $[\text{C}_7\text{H}_{11}\text{N}_2]^+$ , 4%), 153 ( $[\text{bmmim}]^+$ , 100%), 586 ( $[\text{bmmim}][(\text{CF}_3\text{SO}_2)_2\text{N}]^+$ , >1%).  $m/z$  (FAB<sup>-</sup>); 280 ( $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , 100%), 147 ( $[\text{CF}_3\text{SO}_2\text{N}]^-$ , 5%). IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$ ; 3187 (aromatic C–H str., s), 3151 (aromatic C–H str., m), 2968 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H str. asym., m), 2942 ( $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H str. asym., m), 2880 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H str. sym., m), 1591 (aromatic C–C str., m), 1466 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  C–H def., asym., m), 1352 (S–O str., s), 1193 (F–C–F str., s), 1137 (C–F str., s), 843 (aromatic C–H out of plane def., w).<sup>32–34</sup>

#### Preparation of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>])

The same procedure was used as for [bmim][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]. Solvent volumes were scaled as necessary. From 130 g (0.75 mol, 1 equiv.) [bmim]Cl and 90 g (0.82 mol, 1.1 equiv.) sodium tetrafluoroborate, was obtained the title compound as a colourless liquid (128 g, 0.56 mol, 70%).  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  (270 MHz,  $\text{CDCl}_3$ ); 0.94 (3H, t,  $J$  7.3 Hz,  $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.35 (2H, m,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.84 (2H, p,  $J$  7.6 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.94 (3H, s,  $\text{NCH}_3$ ), 4.17 (2H, t,  $J$  7.4 Hz,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.27 (1H, s, C(5)H), 7.31 (1H, s, C(4)H),

8.81 (1H, s, C(2)H).<sup>30</sup> <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta_{\text{C}}$  (270 MHz, CD<sub>3</sub>COCD<sub>3</sub>,  $\delta$ /ppm relative to TMS); 12.51 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.72 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.38 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 35.26 (NCH<sub>3</sub>), 48.85 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 121.90, 123.22 (C(5)H, C(4)H), 136.37 (C(2)H). *m/z* (FAB<sup>+</sup>); 55 ([C<sub>3</sub>H<sub>6</sub>N]<sup>+</sup>, 2%), 83 ([C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>]<sup>+</sup>, 15%), 96 ([C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>]<sup>+</sup>, 4%), 109 ([C<sub>6</sub>H<sub>9</sub>N<sub>2</sub>]<sup>+</sup>, 4%), 139 ([bmim]<sup>+</sup>, 100%), 365 ([bmim]<sub>2</sub>[BF<sub>4</sub>]<sup>+</sup>, 1%).<sup>31</sup> *m/z* (FAB<sup>−</sup>); 19 (F<sup>−</sup>, 83%), 87 ([BF<sub>4</sub>]<sup>−</sup>, 100%), 313 ([bmim][BF<sub>4</sub>]<sub>2</sub><sup>−</sup>, 10%). IR (neat)  $\nu_{\text{max}}$ /cm<sup>−1</sup>; 3162 (aromatic C–H str., m), 3121 (aromatic C–H str., m), 2965 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> C–H str. asym., m), 2939 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> C–H str. asym., m), 2877 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> C–H str. sym., m), 1574 (aromatic C–C str., m), 1466 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> C–H def., asym., m), 1171 (aromatic C–H in plane def., m), 1059 (BF<sub>4</sub>,  $\nu_3$ , s, br.), 754 (BF<sub>4</sub>,  $\nu_1$ , m), 849 (aromatic C–H out of plane def., w).<sup>32,33,35</sup>

### Synthesis of tetrapropylammonium perruthenate ([<sup>n</sup>Pr<sub>4</sub>N][RuO<sub>4</sub>])<sup>36</sup>

Anhydrous Na<sub>2</sub>CO<sub>3</sub> (3.20 g, 30 mmol) and NaBrO<sub>3</sub> (12.00 g, 80 mmol) were dissolved in water (*ca.* 40 cm<sup>3</sup>) and RuCl<sub>3</sub>·*n*H<sub>2</sub>O (0.27 g, 1 mmol) pre-dissolved in water (20 cm<sup>3</sup>) was added with stirring until the colour changed to yellow/green. [<sup>n</sup>Pr<sub>4</sub>][OH] (1 cm<sup>3</sup> of 1 mol dm<sup>−3</sup>) was added with stirring and the deep moss green precipitate that formed extracted into DCM. The solution was dried over anhydrous MgSO<sub>4</sub> and concentrated *in vacuo* to give the title compound as a deep moss green solid 0.45 g (1.28 mmol, 99%). The solid was stored at −18 °C, mp 161 °C (decomp.). UV–VIS spectrum:  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>)[nm( $\epsilon$ /dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>)] 318 (1904), 384 (2261). IR ( $\nu_{\text{max}}$ /cm<sup>−1</sup>): 831 s ( $\nu_{\text{as}}$ (RuO<sub>4</sub>)(lit.,<sup>36</sup> 836)). FAB<sup>+</sup> mass spectrum: *m/z* = 186 ([<sup>n</sup>Pr<sub>4</sub>N]<sup>+</sup>, 100%).

### Typical oxidation procedure with NMO as co-oxidant

This general method was used for all reactions and different alcohols were used. The catalyst (5 mol%) was accurately weighed into a round bottom flask charged with ionic liquid (2 cm<sup>3</sup>), the co-oxidant NMO (3 mmol, 1.5 equiv.) and a magnetic stirrer bar. The mixture was stirred until a homogeneous solution formed. The alcohol (2 mmol, 1 equiv.) was then added and the mixture stirred for 2 hours in an N<sub>2</sub> atmosphere. The product was extracted from the ionic liquid with Et<sub>2</sub>O (3 × 2 cm<sup>3</sup>) and analysed by GC.

### Typical oxidation procedure with O<sub>2</sub> as co-oxidant

A round bottom flask (5 cm<sup>3</sup>) was charged with TPAP (0.035 g, 5 mol% (with respect to substrate)) and a stir bar. The ionic liquid was then added (2 cm<sup>3</sup>) followed by copper(I)chloride (0.010 g, 5 mol%) and 2-aminopyridine (0.047 g, 25 mol%). A suba-seal was placed in the neck of the flask and the flask placed in an oil bath thermostatted at the requisite temperature. The mixture was stirred thoroughly to give a black solution. A syringe was pierced through the suba-seal and placed well below the surface of the liquid. Oxygen was then bubbled through at a rate of approximately one bubble per second. The alcohol was added (2 mmol, 1 equiv.) in one portion to the reaction mixture by syringe through the suba-seal at *t* = 0. At the requisite times aliquots of the reaction mixture were removed and the alcohol and aldehyde extracted with Et<sub>2</sub>O (3 × 2 cm<sup>3</sup>). The ether/reaction product solution was then analysed by GC and GC-MS.

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