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TEMPO and Carboxylic Acid Functionalized Imidazolium Salts/Sodium Nitrite: An Efficient, Reusable, Transition Metal-Free Catalytic System for Aerobic Oxidation of Alcohols

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Abstract: An effective catalytic system comprising a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) functionalized imidazolium salt ([Imim-TEMPO]$^+X^-$), a carboxylic acid substituted imidazolium salt ([Imim-COOH]$^+X^-$), and sodium nitrite ($NaNO_2$) was developed for the aerobic oxidation of aliphatic, allylic, heterocyclic and benzylic alcohols to the respective carbonyl compounds with excellent selectivity up to >99%, even at ambient conditions. Notably, the catalyst system could preferentially oxidize a primary alcohol to the aldehyde rather than a secondary alcohol to the ketone. Moreover, the reaction rate is greatly enhanced when a proper amount of water is present. And a high turnover number (TON 5000) is achieved in the present transition metal-free aerobic catalytic system. Additionally, the functionalized imidazolium salts are successfully reused at least four times. This process thus represents a greener pathway for the aerobic oxidation of alcohols into carbonyl compounds by using the present task-specific ionic liquids in place of the toxic and volatile additive, such as hydrogen bromide, bromine, or hydrogen chloride (HBr, Br_2 or HCl), which is commonly required for the transition metal-free aerobic oxidation of alcohols.

Keywords: alcohol oxidation; imidazolium salts; molecular oxygen; 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO); water

Introduction

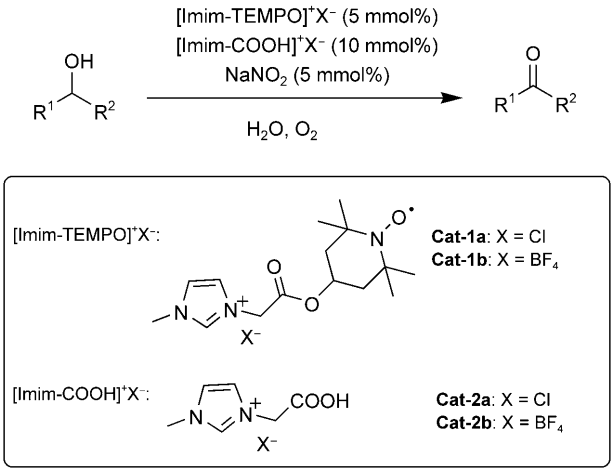
The selective oxidation of primary and secondary alcohols into the corresponding aldehydes or ketones is undoubtedly one of the most important and challenging transformations in organic chemistry.[1] And one of particular interest in this field is the use of the stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in combination with terminal oxidants.[2] However, the many systems that exist could suffer from the large amounts of waste produced because stoichiometric amounts of terminal oxidants such as bleach, sodium chlorite, *m*-chloroperoxybenzoic acid (*m*-CPBA), hypervalent iodine(III) compounds has been used.[3] From economic and environmental perspectives, using molecular oxygen or hydrogen peroxide as a terminal oxidant has received great attention nowadays since only water as a sole by-product is formed.

Transition metals like copper, ruthenium, iron in conjugation with TEMPO have been reported for the oxidation of alcohols under the aerobic conditions.[4] However, deactivation of the transition metal catalysts and product contamination with heavy metals hinder the development of these systems.[5] Therefore, developing a transition metal-free system for aerobic oxidations would be promising from the viewpoint of *green chemistry* and *sustainable development*. In this context, Liang and Hu et al. made a great breakthrough in this field. At first, they developed three-component catalyst systems, including TEMPO/Br_2/$NaNO_2$,[6] TEMPO/1,3-dibromo-5,5-dimethylhydantoin/$NaNO_2$,[7] TEMPO/HCl/$NaNO_2$,[8] TEMPO/HBr/*tert*-butyl nitrite (TBN),[9] which would be considered to go through a sequential tricycle with a two-electron transfer mechanism. Then, a TEMPO/TBN double-component and sequential bicycle catalyst system was successfully exploited for alcohol oxidations, and even has been applicable to substrates containing acid-sen-

sitive functional groups without the need of the toxic halogen source and acid.[10] The TEMPO used could not be recovered, however. On the other hand, Karimi et al. developed a heterogeneous catalyst system, consisting of the SBA-15-supported TEMPO/$Bu_4NBr/NaNO_2$ under acidic conditions, allowing the supported TEMPO to be recoverable.[11] In addition, the acidic conditions were essential to the reaction when $NaNO_2$ was used as the NO source. And certain toxic and high volatile substances, such as HBr, Br_2, HCl, CH_3COOH, are commonly needed for this transition metal-free aerobic oxidation according to the literature. Consequently, it is still desirable to develop a cleaner, highly efficient and recyclable homogeneous catalyst system without the need of a transition metal for this process.

Ionic liquids as an environmentally friendly solvent represent interesting properties such as high thermal stability, negligible vapor pressure, high loading capacity and easy recyclability. Various chemical reactions have been well performed in ionic liquids. Moreover, the task-specific ionic liquid could be designed for specific purposes on the basis of the reaction mechanism.[12] However, only a few reports about TEMPO functionalized imidazolium salts for alcohol oxidations are available in the literature.[13] Meanwhile, acidic ionic liquids also have attracted much attention.[14]

A three-component catalyst system, consisting of a TEMPO functionalized imidazolium salt ([Imim-TEMPO]$^+X^-$, **Cat-1a** or **Cat-1b**), a carboxylic acid substituted imidazolium-based ionic liquid ([Imim-COOH]$^+X^-$, **Cat-2a** or **Cat-2b**) to provide the acidic conditions, and $NaNO_2$ as the NO resource to activate oxygen, was designed for the aerobic oxidation of alcohols in water (Scheme 1). To our delight, the catalyst system ([Imim-TEMPO]$^+X^-$/[Imim-COOH]$^+X^-$/$NaNO_2$) was effective and highly selective (almost



Scheme 1. Aerobic oxidation of alcohol catalyzed by [Imim-TEMPO]$^+X^-$/[Imim-COOH]$^+X^-$/$NaNO_2$.

>99%) for the oxidation of aliphatic, allylic, heterocyclic and benzylic alcohols to the respective carbonyl compounds, even at ambient conditions.

Results and Discussion

The exploratory experiments were started by screening the designed catalyst system **Cat-1a**/**Cat-2a**/$NaNO_2$. And benzyl alcohol was chosen as a model substrate. The results are summarized in Table 1. It is found that **Cat-1a**, **Cat-2a**, $NaNO_2$ and oxygen were essential for the aerobic oxidation of benzyl alcohol (Table 1, entries 1–4). However, the yield of benzyl aldehyde was just 21% in the absence of water (entry 5). Interestingly, a 53% yield was obtained as a result of adding 0.05 mL water (entry 6), presumably due to an improvement of the solubility of the catalyst system and an acceleration of the ionization of the **Cat-2** in water.

In this respect, control experiments were carried out in aprotic solvents like DMSO (dimethyl sulfoxide) and DMF (*N,N*-dimethylformamide). DMSO which is capable of forming a homogeneous system enhanced the reaction (entry 9), whereas DMF could not dissolve the catalyst and demonstrated a poor performance under identical conditions (entry 10). Consequently, the solubility of the catalyst would likely be more important for this reaction in comparison with the ionizing ability of the **Cat-2a**. Notably, the oxidation could also be successfully carried out under mild conditions, even at room temperature and an air atmosphere (entries 7 and 8). Moreover, the effect of the **Cat-1a** loading was evaluated (entries 11–16). The reaction was completed within 30 min in the presence of 5% catalyst **Cat-1a** (entry 11). The reaction was operative in the range of the catalyst loading from 1 to 0.01% (entries 12 to 15). Specifically, a high turnover number (TON 5000) can be also attained (entry 16).

The initial results showed that water played an accelerative effect for the aerobic oxidation. Accordingly, the effect of the quantity of water was examined. The yield and selectivity were found to be at the same level when the amount of water was altered from 0.05 mL to 0.2 mL (Table 2, entries 3–5). However, a more or a lesser amount of water can lead to a drop of the yield (entries 1, 2, 6 and 7). This is reasonable that the catalysts could not be completely dissolved if the added water is not enough, and thus retarded the ionization of **Cat-2a**, and therefore resulted in a decrease in the yield. On the other hand, an excessive amount of water could form an obvious biphasic system, that is catalysts/H_2O with the substrate, leading to the decrease in yield.

To examine the utility and generality of the catalyst system for the alcohol oxidation, we applied the new catalyst system to a variety of alcohols, and the results

Table 1. Aerobic oxidation of alcohol catalyzed by $[Imim\text{-}TEMPO]^+X^-/[Imim\text{-}COOH]^+X^-/NaNO_2$.[a]

Entry	P_{O_2} [MPa]	Amount of **Cat-1a** [mol%]	Amount of **Cat-2a** [mol%]	Solvent	T [K]	t [h]	Conv. [%][b]	Yield [%][b]	TON
1	1	–	10	–	333	0.25	–	–	–
2[c]	1	5	10	–	333	0.25	–	–	–
3	1	5	–	–	333	0.25	–	–	–
4	–	5	10	–	333	0.25	-	–	–
5	1	5	10	–	333	0.25	21	21	4
6	1	5	10	H_2O	333	0.25	53	53	10
7	0.1	5	10	H_2O	303	6	25	25	5
8[d]	–	5	10	H_2O	303	8	17	17	3
9	1	5	10	DMSO	333	0.25	71	71	14
10	1	5	10	DMF	333	0.25	39	39	8
11	1	5	10	H_2O	333	0.5	100	>99	20
12	1	1	10	H_2O	333	0.5	40	40	40
13	1	0.5	10	H_2O	333	2	88	84	168
14[e]	1	0.1	10	H_2O	333	3	66	66	660
15[f]	1	0.01	10	H_2O	333	24	23	22	2200
16[g]	1	0.001	10	H_2O	333	36	5	5	5000
17[h]	1	5	10	H_2O	333	0.25	48	48	9.6
18[i]	1	5 (**Cat-1b**)	5 (**Cat-2b**)	H_2O	333	0.25	49	49	9.8

[a] Unless otherwise noted, all the experiments were carried out with benzyl alcohol (0.2 mL, 1.93 mmol), $NaNO_2$ (6.7 mg, 5 mol%).
[b] Determined by GC using biphenyl as an internal standard.
[c] Without $NaNO_2$.
[d] 1 atm of air.
[e] Benzyl alcohol (1 mL, 9.65 mmol), $NaNO_2$ (33.5 mg, 5 mol%).
[f] Benzyl alcohol (4 mL, 48.25 mmol), $NaNO_2$ (167.5 mg, 5 mol%).
[g] Benzyl alcohol (5 mL, 48.25 mmol), $NaNO_2$ (167.5 mg, 5 mol%).
[h] NaCl (11.2 mg, 10 mol%) was added.
[i] **Cat-1b** (36.9 mg, 5 mol%)/**Cat-2b** (44.0 mg, 10 mol%) was used instead of **Cat-1a**/**Cat-2a**.

Table 2. Effect of the amount of water.[a]

Entry	V_{H_2O} [mL]	Conv. [%][b]	Yield [%][b]
1	1	16	16
2	0.5	29	29
3	0.2	47	47
4	0.1	51	51
5	0.05	53	53
6	0.025	16	16
7	0.01	15	15

[a] Reaction conditions: benzyl alcohol (0.2 mL, 1.93 mmol), **Cat-1a** (31.9 mg, 5 mol%), **Cat-2a** (34.0 mg, 10 mol%), $NaNO_2$ (6.7 mg, 5 mol%), $P_{O_2}=1$ MPa, $T=333$ K, $t=15$ min.
[b] Determined by GC using biphenyl as an internal standard.

are summarized in Table 3. Obviously, the activities of primary benzylic alcohols were best, and the activities of those primary benzylic alcohols were also not significantly affected by the electronic properties and steric hindrance of the substituents on the benzene ring (Table 3, entries 1–7). Even substrates with an *o*- or *p*-nitro group showed good activity at an elevated temperature (entry 9 *vs.* 8, 10). In addition, the reactivity of secondary benzylic alcohols, such as 1-phenylethanol, benzhydrol, was affected by the α substituent group due to steric hindrance. And both substrates could be smoothly oxidized to the corresponding acetophenone and benzophenone, respectively, after prolonging the reaction time compared with the primary benzylic alcohols (entries 11 and 12). Besides, the catalytic system was applicable to the oxidation of other activated primary alcohols such as allylic, heterocyclic alcohols (entries 13 and 14). To our delight, aliphatic alcohols could be converted to the target products with high selectivity. Unfortunately, the oxidations of 1-heptanol and 2-octanol were unsatisfactory even after elongating the reaction time because of the further oxidation of the corresponding aldehydes into acids and/or ortho esters (entries 16 and 23).[15] Moreover, in the cases of aliphatic alcohols, the reaction rate also relied on the steric hindrance as well as the chain length (entries 15–24). The longer the chain was, poorer was the activity (entries 15–20). In order to examine the chemoselectivity of the catalytic system, a 1:1 molar mixture of primary and secondary alcohols was used in the present catalytic system. Interestingly, only primary alcohols, such as benzyl alcohol and 1-heptanol were converted into

Table 3. Catalytic aerobic oxidation for various alcohols.[a]

Entry	Substrate	Product	T [K]	Time	Conv. [%][b]	Yield [%][b]
1	Benzyl alcohol	Benzyl aldehyde	333	30 min	100	>99
2			373	10 min	100	>99
3	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	333	1 h	97	96
4			373	20 min	54	53
5	2-Methoxybenzyl alcohol	2-Methoxybenzaldehyde	333	30 min	87	85
6	3-Methoxybenzyl alcohol	3-Methoxy benzaldehyde	333	30 min	80	78
7	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	333	20 min	93	92
8	4-Nitro benzyl alcohol	4-Nitrobenzaldehyde	353	1 h	26	23
9			373	20 min	94	94
10	2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	353	1 h	72	72
11	1-Phenylethanol	Acetophenone	333	3 h	100	96
12	Benzhydrol	Benzophenone	353	12 h	68	66
13[c]	2-Furfurylmethanol	Furfuryl aldehyde	333	1 h	100	93
14	Cinnamyl alcohol	Cinnamaldehyde	333	6 h	24	22
15[c]	1-Heptanol	1-Heptaldehyde	333	6 h	51	45
16[c]			333	12 h	94	76[d]
17	Dodecanol	Dodecanal	333	6 h	36	35
18			333	12 h	79	72
19	1-Hexadecanol	1-Hexadecanal	333	6 h	6	6
20			333	12 h	45	41
21[c]	2-Phenyl ethanol	Phenylacetaldehyde	333	6 h	59	56
22[c]	2-Octanol	2-Octanone	333	6 h	29	23
23[c]			333	12 h	81	66[e]
24[c]	Cyclohexanol	Cyclohexanone	333	6 h	26	26
25[c]	4-Methoxybenzyl alcohol + 1-Phenylethanol	4-Methoxybenzyl aldehyde + Acetophenone	333	30 min	62 + 3	62 + 2
26[c]	1-Heptanol + Cyclohexanol	1-Heptaldehyde + Cyclohexanone	333	5 h	35 + 0	34 + 0

[a] *Reaction conditions:* alcohol (1.93 mmol), **Cat-1a** (31.9 mg, 5 mol%), **Cat-2a** (34.0 mg, 10 mol%), $NaNO_2$ (6.7 mg, 5 mol%), $V_{H_2O} = 0.05$ mL; $P_{O_2} = 1$ MPa, $T = 333$ K.
[b] Isolated yield.
[c] Determined by GC.
[d] 12% acid.
[e] 5% isooctyl acid and 5% isooctyl isooctanoate were observed.

the corresponding aldehydes, and the secondary alcohols were almost completely recovered (entries 25 and 26).

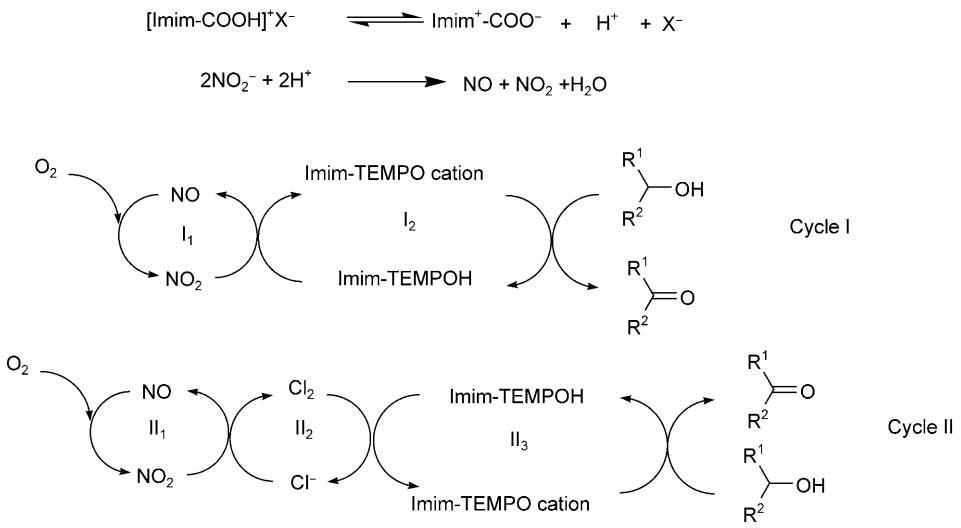
Next, we examined the recyclability of this catalyst system (Table 4). In each cycle, the catalysts were dissolved in water, and the product could be extracted by diethyl ether or supercritical carbon dioxide. After being recovered, the catalyst, the fresh substrate, i.e., 2-nitrobenzyl alcohol was used for the second run (Table 4, entry 2), and the substrate was almost completely recovered. This is probably because $NaNO_2$ would decompose into NO and NO_2 under the acidic conditions, and be lost at the stage of product separation.[6,7,8] In this regard, $NaNO_2$ was replenished for the subsequent run. The results showed that the yield and selectivity of the products just had a slight decrease after the fourth run (entries 4–6). As a result, the functionalized imidazolium salts are successfully reused at least four times.

Based on previous studies[6–11] and the above-mentioned results, a tentative mechanism of this aerobic

Table 4. Recycling of **Cat-1a** and **Cat-2a**.[a]

Entry	Conv. [%][b]	Yield [%][b]
1	52	52
2[a]	2	1
3	53	52
4[d]	49	49
5[e]	48	47
6[f]	43	43

[a] The procedure for recycling the catalyst system is given in the Experimental Section. *Reaction conditions:* 2-nitrobenzyl alcohol (1.93 mmol), **Cat-1a** (31.9 mg, 5 mol%), **Cat-2a** (34.0 mg, 10 mol%), $NaNO_2$ (6.7 mg, 5 mol%), $V_{H_2O} = 0.5$ mL; $P_{O_2} = 1$ MPa, $T = 333$ K.
[b] Isolated yield.
[c] The second run after entry 1.
[d] The second run after entry 3 and $NaNO_2$ (6.7 mg, 5 mol%) was added.
[e] The third run after entry 3 and $NaNO_2$ (6.7 mg, 5 mol%) was added.
[f] The fourth run after entry 3 and $NaNO_2$ (6.7 mg, 5 mol%) was added.



Scheme 2. The proposed mechanism.

oxidation is proposed as shown in Scheme 2. The designed transition metal-free aerobic system was completed by a sequential bicycle (cycle I) or tricycle (cycle II) involving a two-electron transfer step. Indeed, the control experiments showed that the chloride anion gave a comparable activity with BF_4^- (Table 1, entry 18 *vs.* 6), whereas increasing the concentration of chloride anion had no effect on the reaction (Table 1, entry 17 *vs.* 6). In other words, cycle I was necessary. On the other hand, as shown in Scheme 2, NO_2^- could release NO and NO_2 under acidic conditions, and the oxidation of NO into NO_2 could proceed easily with molecular oxygen. In this context, the experimental results for reusing the catalytic system showed the fresh $NaNO_2$ must necessarily be added for the subsequent run as discussed above (Table 4, entries 4–6), suggesting the existence of the essential process (I_1 and II_2), so that the NO_2 produced could oxidize the chorine anion to Cl_2 (II_2) or TEMPOH to oxoammonium cation (I_2).

Conclusions

A three-component catalyst system, consisting of TEMPO functionalized imidazolium salt, carboxylic acid functionalized imidazolium salt and $NaNO_2$, was developed for the aerobic oxidation of alcohols with avoidance of using a toxic and high volatile substance, such as HBr, Br_2, or HCl. The present homogeneous catalyst system was recyclable, highly efficient and selective for a wide set of aliphatic, allylic, heterocyclic and benzylic alcohols, even at ambient conditions. This process thus represents a greener pathway for aerobic oxidation of alcohols into carbonyl compounds by using the present task-specific ionic liquids without the need of a transition metal.

Experimental Section

General Information

NMR spectra were recorded on a Bruker 300 or 400 spectrometer in $CDCl_3$ or D_2O. ^1H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to TMS. ^1H and ^{13}C NMR positive chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: $\delta_C = 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H = 7.26$ ppm). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC-MS were measured on a Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m × 0.25 μm) using a flame ionization detector. Column chromatography was performed by using silica gel 200–300 mesh with ethyl acetate/petroleum as eluent. And melting points were measured on an X4 apparatus and uncorrected.

Chemical Reagents

Alcohols were purchased from Alfa Aesar Company. 1-Methylimidazole, ethyl chloroacetate, chloroacetic acid and hydrochloric acid (37%) were purchased from Tianjin Guangfu Fine Chemical Research Institute. 4-Hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl from Liansheng Chemical Company of Jiangsu province was used without further purification. $NaBF_4$ was purchased from Hengye Zhongyuan Chemical Research Institute. The other organic compounds from the sixth reagent company of Tianjin were used without further purification except for the solvents, which were distilled by the known procedure prior to use.

Preparation and Characterization of [Imim-TEMPO]$^+$X$^-$[13,16]

Procedure for preparation of Cat-1a: To a stirred solution of 4-hydroxy-2,2,6,6-tetramethylpiperdine-1-oxyl (**1**, 4.3 g, 25 mmol) and chloroactic acid (2.0 g, 25 mmol) in CH_2Cl_2 (80 mL) at 0 °C under argon, DCC (5.15 g, 25 mmol) and DMAP (0.75 g, 6.25 mmol) were dropwise added. And the

mixture was stirred for 12 h at room temperature. After reaction, the precipitate was filtered, and the filtrate was washed with 1 M HCl (25 mL), saturated $NaHCO_3$ (50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$, and evaporated under reduced pressure. Further purification was through a short flash chromatography (the eluent: EtOAc-petroleum ether 1:10) providing 2,2,6,6-tetramethyl-1-oxyl-piperidin-4-yl 2-chloroacetate (**2**) as a red powder. Then 1-methylimidazole (0.46 g, 5.6 mmol) was added to a solution of **2** (1.00 g, 4 mmol) in MeCN (30 mL), and the resulting solution was stirred for 48 h at 80 °C. After concentration to about half the original volume, diethyl ether was added to get a precipitate. Then the solid was filtered and washed with acetone, diethyl ether, respectively to give **Cat-1a** as a light red powder; yield: 76%.

Procedure for preparation of Cat-1b: A round-bottomed flask was charged with 0.4132 g (1.25 mmol) of **Cat-1a**, 0.1373 g (1.25 mmol%) of $NaBF_4$ in 1 mL of distilled water. The reaction mixture was stirred at room temperature for 4 h affording a heterogeneous mixture. The water was removed under reduced pressure and then 1 mL of dichloromethane was added. The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure to afford **Cat-1b** as a red powder. One drop of neat phenylhydrazine was added into the samples containing the nitroxyl radical prior to NMR analysis in order to reduce *in situ* the paramagnetic center to the corresponding hydroxylamine species.

1-Hydroxy-2, 2, 6, 6-tetramethylpiperidin-4-yl 2-chloroacetate: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.18$ (s, 12 H), 1.58 (t, $^3J_{H,H} = 12$ Hz, 2 H), 1.93 (d, $^3J_{H,H} = 5.4$ Hz, 2 H), 3.98 (s, 2 H), 5.08–5.14 (m, 1 H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta =$ 20.4, 31.7, 40.9, 43.5, 58.9, 69.0, 166.7.

Cat-1a-TEMPOH: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.13$ (s, 12 H), 1.37 (t, $^3J_{H,H} = 9$ Hz, 1 H), 1.59 (t, $^3J_{H,H} = 9$ Hz, 2 H), 1.96 (t, $^3J_{H,H} = 9$ Hz, 2 H), 3.98 (s, 3 H), 5.05 (s, 1 H), 5.11–5.21 (m, 2 H), 7.40 (s, 2 H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 20.8$, 29.8, 36.0, 42.2, 50.0,60.2, 70.0, 123.5, 123.6, 128.4, 167.4.

Cat-1a: mp 213–216 °C (Ref.[13b]: mp 225–227 °C); ESI-MS (4.8 kV): m/z (%) = 295 (100) $[M-Cl]^+$.

Cat-1b-TEMPOH: ^{1}H NMR (400 MHz, D_2O): $\delta = 1.10$ (s, 12 H), 1.57 (t, $^3J_{H,H} = 12$ Hz, 2 H), 1.94 (t, $^3J_{H,H} = 11.2$ Hz, 2 H), 3.76 (s, 3 H), 4.97 (s, 2 H), 5.11 (m, 1 H), 7.32(s, 2 H); ^{13}C {H} NMR (100.6 MHz, D_2O): $\delta = 20.7$, 30.0, 35.8, 42.1, 49.8, 60.1, 69.8, 123.3, 123.5, 128.5, 167.3.

Preparation and Characterization of [Imim-COOH]$^+$X$^-$[14]

Under an inert atmosphere of argon, a mixture of 1-methylimidazole (0.020 mol) and $ClCH_2COOCH_3$ (0.020 mol) was stirred at room temperature for 6 h. The resultant mixture turned to a solid during the reaction. The solid was washed with diethyl ether (3 × 30 mL) and dried under vacuum for 24 h to give 1-ethoxycarbonylmethyl-3-methylimidazolium chloride (**3**). In a typical procedure, a mixture of **3** (0.020 mol) and 37% HCl aqueous solution (0.022 mol) was refluxed for 4 h. The solvent was removed and the residue was washed with acetone and diethyl ether to give the product as a white powder **Cat-2a**.

The synthetic procedure of **Cat-2b** is similar to the procedure for **Cat-1b**.

3: ^{1}H NMR (300 MHz, D_2O): $\delta = 1.22$ (t, $^3J_{H,H} = 7.2$ Hz, 3 H), 3.88 (s, 3 H), 4.23 (q, 2 H), 5.10 (s, 2 H), 7.45 (s, 2 H), 8.76 (s, 1 H); ^{13}C NMR (75 MHz, D_2O): $\delta = 13.3$, 36.1, 50.0, 63.7, 123.6, 137.5, 168.3.

Cat-2a: mp 191–193 °C (Ref.[16]: 204 °C); ^{1}H NMR (300 MHz, D_2O): $\delta = 3.82$ (s, 3 H), 5.03 (s, 2 H), 7.40 (d, $^3J_{H,H} = 2.7$ Hz), 8.70 (s, 1 H); ^{13}C NMR (75 MHz, D_2O): $\delta =$ 36.09, 50.0, 123.6, 137.4, 169.9; ESI-MS (4.8 kV): m/z (%) = 141 (100) $[M-Cl]^+$.

Cat-2b: ^{1}H NMR (300 MHz, D_2O): $\delta = 3.85$ (s, 3 H), 5.01 (s, 2 H), 7.40 (s, 2 H), 8.69 (s, 1 H); ^{13}C NMR (75 MHz, D_2O): $\delta = 36.0$, 50.2, 123.5, 137.4, 170.3.

Representative Procedure for the Aerobic Oxidation of Alcohols

***Safety Warning**: Experiments using oxygen are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.*

A mixture of substrate (1.93 mmol), **Cat-1a** (31.9 mg, 5 mol%), **Cat-2a** (34.0 mg, 10 mol%), $NaNO_2$ (6.7 mg, 5 mol%) and 0.05 mL water was placed in a 25-mL autoclave equipped with an inner glass tube. 1 MPa O_2 was introduced into the autoclave and the system was heated to the reaction temperature. The mixture was stirred continuously for the designated reaction time. After cooling, products were then extracted by diethyl ether, and analyzed by gas chromatography (Shimadzu-2014) equipped with a capillary column (RTX-5 30 m × 0.25 μm) using a flame ionization detector. The structure and the purity of the products were further identified using NMR (Bruker-300 MHz, 400 MHz), GC-MS (HP G1800 A), HPLC-MS (LCQ Advantage) and GC, HPLC by comparing retention times and fragmentation patterns with those of authentic samples.

Procedure for Reusing the Task-Specific Ionic Liquids

After the addition of diethyl ether (10 mL × 3) to the resulting mixture upon completion of the reaction, the aqueous layer containing the catalyst was separated by simple decantation of the ether phase containing the oxidized products. Consequently, the aqueous phase containing the catalyst was bubbled with argon. We conducted further oxidations by the addition of successive portions of 2-nitrobenzyl alcohol and $NaNO_2$ to the water phase followed by stirring under identical reaction conditions.

Benzaldehyde: Light yellow oil liquid, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.50$ (t, $^3J_{H,H} = 7.7$ Hz, 2 H), 7.60 (t, $^3J_{H,H} =$ 7.4 Hz, 1 H), 7.84 (d, $^3J_{H,H} = 7.9$ Hz, 2 H), 9.98 (s, 1 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 100.6 MHz): $\delta = 128.9$, 129.6, 134.3, 136.2, 192.3.

4-Methoxybenzaldehyde: Colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.87$(s, 3 H), 7.00 (d, $^3J_{H,H} = 8.72$ Hz, 2 H), 7.82 (d, $^3J_{H,H} = 8.78$ Hz, 5 H), 9.87 (s, 1 H, CHO); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): $\delta = 55.5$, 114.3, 130.0, 131.9, 164.6, 190.7.

2-Methoxybenzaldehyde: Light yellow solid, mp 36–38 °C, ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.84$ (s, 3 H), 6.94 (m, 2 H), 7.48 (t, $^3J_{H,H} = 8.4$ Hz, 1 H), 7.75 (d, $^3J_{H,H} = 3.9$ Hz, 1 H), 10.4

(s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 55.4$, 111.5, 120.4, 124.6, 128.2, 135.8, 161.6, 189.5.

3-Methoxybenzaldehyde: Light yellow oil liquid, ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.83$(s, 3H), 7.14 (m, 1H), 7.36 (d, $^3J_{H,H} = 1.05$ Hz, 1H), 7.42 (m, 2H), 9.94 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 55.3$, 112.0, 121.3, 123.4, 129.9, 137.7, 160.1, 192.0.

4-Methylbenzaldehyde: Colorless liquid, ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.44$ (s, 3H), 7.33 (d, $^3J_{H,H} = 3.9$ Hz, 2H), 7.78 (d, $^3J_{H,H} = 4.05$ Hz, 2H), 9.97 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 21.9$, 129.7, 129.9, 134.2, 145.6, 192.0.

4-Nitrobenzaldehyde: Light yellow acicular crystals, mp 105–106 °C, ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 8.08$ (d, $^3J_{H,H} =$ 4.35 Hz, 2H), 8.39 (d, $^3J_{H,H} = 4.35$ Hz, 2H), 10.16 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) : $\delta = 124.2$, 130.4, 140.0, 151.1, 190.2.

2-Nitrobenzaldehyde: Light yellow solid, mp 45–46 °C, ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.78$ (m, 2H), 7.96 (d, $^3J_{H,H} = 2.7$ Hz, 1H), 8.13 (d, $^3J_{H,H} = 3$ Hz, 1H), 10.43 (s, 1H); $^{13}C\{1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta = 124.5$, 129.6, 131.4, 134.1, 188.1.

Acetophenone: Light yellow liquid, ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.60$ (s, 3H), 7.46 (t, $^3J_{H,H} = 7.7$ Hz, 2H), 7.56 (t, $^3J_{H,H} = 7.5$ Hz, 1H), 7.96 (d, $^3J_{H,H} = 7.8$ Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): $\delta = 26.5$, 128.2, 128.5, 133.0, 137.1, 198.1.

Benzophenone: White crystals, mp 47–48 °C, ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$ (t, $^3J_{H,H} = 7.9$ Hz, 4H), 7.58 (t, $^3J_{H,H} = 7.9$ Hz, 2H), 7.81 (t, $^3J_{H,H} = 5.7$ Hz, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 128.3$, 130.1, 132.4, 137.6, 196.7.

Cinnamaldehyde: Light yellow liquid, ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.69$–6.77 (m, 1H), 7.43–7.47 (m, 4H), 7.52–7.59 (m, 2H), 9.71 (d, $^3J_{H,H} = 3.9$ Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 128.5$, 128.6, 129.1, 131.3, 134.0, 152.8, 193.8.

Dodecanal: White solid, mp 43–44 °C, ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (s, $^3J_{H,H} = 5.1$ Hz, 3H), 1.25–1.28 (m, 16H), 1.61 (t, $^3J_{H,H} = 5.4$ Hz, 2H), 2.38–2.42 (m, 2H), 9.75 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.1, 22.6, 29.1, 29.2, 29.3, 29.4, 29.6, 31.9, 43.9, 202.9.

1-Hexadecanal: White solid, 33–35 °C, ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.87$ (s, $^3J_{H,H} = 6.9$ Hz, 3H), 1.19–1.28 (m, 24H), 1.62 (t, $^3J_{H,H} = 7.2$ Hz, 2H), 2.39–2.44 (m, 2H), 9.76 (t, $^3J_{H,H} = 2.1$ Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.1, 22.7, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 43.9, 202.9.

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