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Clean and selective oxidation of alcohols catalyzed by ion-supported TEMPO in water

Weixing Qian, Erlei Jin, Weiliang Bao* and Yongmin Zhang

Department of Chemistry, Xi Xi Campus, Zhejiang University, Hangzhou, Zhejiang 310028, People's Republic of China

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Abstract—Three different types of ion-supported TEMPO catalysts are synthesized and their catalytic activity in the chemoselective oxidation of alcohols is investigated. These new catalysts show high catalytic activity in water and can be reused for the next run by extraction of products. Recycling experiments exhibit that ion-supported TEMPO can be reused up to five times without loss of catalytic activity. This system offers a very clean, convenient, environmentally benign method for the selective oxidation of alcohols.

1. Introduction

Chemoselective oxidation of alcohols to carbonyl compounds is an important reaction in organic synthesis and many methods for this transformation have been documented in the literature in view of its importance.[1] Recently the use of metal-free catalysts for selective oxidation of organic compounds is attracting more and more attention because these metal-free catalysts are beneficial from both economic and environmental viewpoints. Moreover, they are readily able to tether to a support covalently and obviate the problem of metal leaching.[2] In the area of metal-free catalytic alcohol oxidations stable free nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), play an increasingly important role in organic synthesis.[3] Usually, efficient methods for the transformation of alcohols to carbonyl compounds or carboxylic acids under mild conditions include the use of 1 mol% of TEMPO as a catalyst and a stoichiometric amount of a terminal oxidant. Many different terminal oxidants have been developed in this reaction including sodium hypochlorite,[4] [bis(acetoxy)iodo]benzene,[5] *m*-CPBA,[6] sodium bromite,[7] trichloroisocyanuric acid,[8] oxone,[9] iodine[10] and oxygen in combination with CuCl[11] or $NaNO_2$.[12] Although these oxidants are successful for efficient alcohol oxidation, separation of the TEMPO from products needs tedious workup procedures. To simplify the product isolation and catalyst recovery the use of polymer-supported catalysts seems alternative. Various polymer-supported TEMPO or its derivatives have been synthesized either based on inorganic[13] or organic supports.[4a,b,14] This polymer-supported TEMPO, however, in some cases will result in decreasing activity or extending reaction time after recycling.[4a,15]

In the last decade ionic liquids have attracted considerable attention as an alternative reaction medium, which represents interesting properties such as high thermal stability, negligible vapor pressure, high loading capacity and easy recyclability. Various chemical reactions can be performed in ionic liquids.[16] One of the attractive features of ionic liquids in organic synthesis is that the structures with the cationic or anionic components can be modified according to requirement, so that they can be adapted to special applications. Recently, increasing attention has been focused on the use of ionic liquids as a means of immobilizing catalysts, facilitating products separation and providing an alternative to recycle the catalysts, and several publications that present their potential in catalysis have been demonstrated.[17] More recently, a TEMPO-derived task-specific ionic liquid for oxidation of alcohols by the Anelli protocol has been described.[18] In this paper, we wish to report three different types of ion-supported TEMPO catalysts for the oxidation of alcohols by an ion-supported hypervalent iodine reagent 1-(4-diacetoxyiodobenzyl)-3-methyl imidazolium tetrafluoroborate[19] $[dibmin]^+[BF_4]^-$ in water and examine their catalytic activity in different cases.

2. Results and discussion

The route for the synthesis of ion-supported TEMPO catalysts was depicted in Scheme 1. Starting from the commercially available 4-hydroxyl-TEMPO (**1**), reaction

Keywords: Alcohols; Oxidation; Ion-supported TEMPO; Catalysis; Hypervalent iodine reagent.
* Corresponding author. Tel./fax: +86 571 88911554; e-mail: wlbao@css.zju.edu.cn

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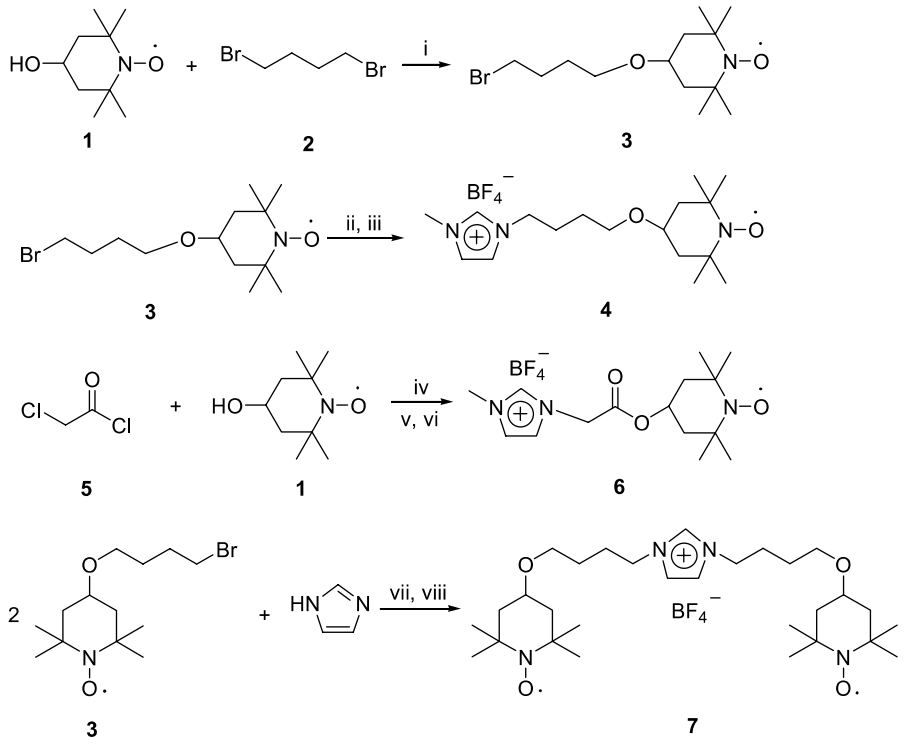
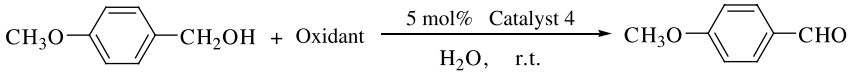


Scheme 1. Synthesis of ion-supported catalysts **4**, **6**, and **7**. Reaction conditions: (i) 1.0 equiv NaH, 1.5 equiv 1,4-dibromobutane, acetone, rt, 25%; (ii) 1.1 equiv 1-methylimidazole, CH_3CN, 60 °C, 97%; (iii) 1.5 equiv $NaBF_4$, acetone, refluxing, 86%; (iv) 1.1 equiv 2-chloroacetyl chloride, 1.1 equiv pyridine, CH_2Cl_2, 5 °C to rt, 80%; (v) 1.1 equiv 1-methylimidazole, CH_3CN, 60 °C, 98%; (vi) 1.5 equiv $NaBF_4$, acetone, refluxing, 85%; (vii) 1.1 equiv imidazole, 1.1 equiv K_2CO_3, acetone, rt; (viii) 1.1 equiv $NaBF_4$, 82%.

with 1,4-dibromobutane (**2**) as a linker in acetone afforded 4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide (**3**) in 25% yield.[20] Quaternization of 1-methylimidazole with **3** and subsequent anion exchange with $NaBF_4$ gave the desired ion-supported TEMPO catalyst (**4**) in 97 and 86% yields, respectively. To raise the yield in the first step, catalyst (**6**) was synthesized with chloroacetyl chloride (**5**) as a linker instead of 1,4-dibromobutane **2** and the yield reached to 80%. The rest steps were analogous to the catalyst **4**. As to symmetrical catalyst (**7**), we wanted to make imidazolium cation have higher loading capacity, reaction of imidazole with 2 equiv bromide **3** in the presence of K_2CO_3 and subsequent metathesis with $NaBF_4$ in one pot afforded the ion-supported diradical **7** in good yield, which was purified by silica gel chromatography. These ion-supported catalysts are insoluble in low polar organic solvents such as ethers or hexanes but are soluble in CH_2Cl_2 and highly soluble in water and ionic liquids. They are ideal candidates for aqueous homogeneous catalysis.

After three ion-supported TEMPO catalysts were obtained, the catalyst **4** was chosen as a candidate to investigate its catalytic activity in combination with various terminal oxidants in water.[21] Table 1 listed the results. The ion-supported TEMPO catalyst **4** proved to be an effective one for the selective oxidation of 4-methoxylbenzyl alcohol except for oxidant peracetic acid, giving 4-methoxylbenzyl aldehyde in good to excellent yields and short reaction times under mild conditions (a 1:1.2 ratio of alcohol/oxidant). It showed similar catalytic activity to that of free TEMPO (Table 1, entry 6). Using $PhI(OAc)_2$ as a terminal oxidant, the reaction did not work well because of poor solubility of $PhI(OAc)_2$ in water. Both I_2 and NaOCl showed effective oxidants. The reaction proceeded fast and gave excellent yields. However, in the case of I_2, a slight

Table 1. Oxidation of 4-methoxybenzyl alcohol catalyzed by an ion-supported TEMPO **4** in water



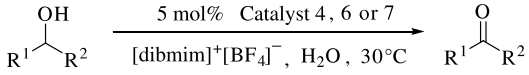
Entry	Oxidant	Time (min)	Yield (%)[a]
1	CH_3CO_3H	600	25
2	$PhI(OAc)_2$	120	70
3	I_2	40	98
4	NaOCl	3	96
5	$[dibmim]^+[BF_4]^-$	6	98
6	$[dibmim]^+[BF_4]^-$	6	97[b]

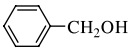
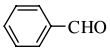
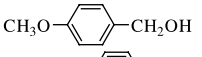
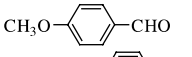
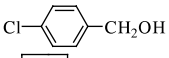
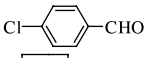
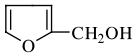
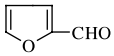
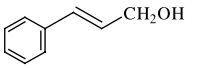
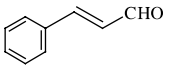
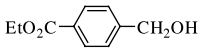
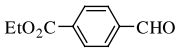
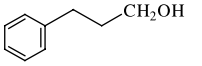
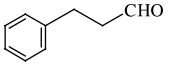
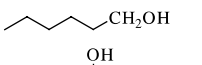
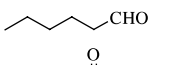
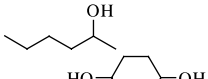
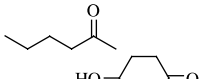
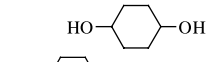
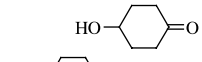
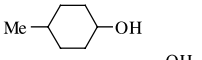
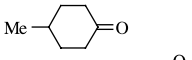
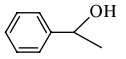
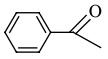
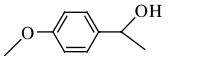
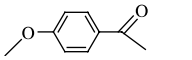
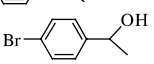
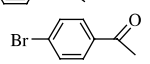
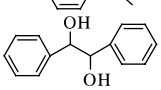
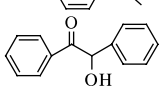
[a] Isolated yields after chromatographic purification unless otherwise noted.
[b] Free TEMPO was used as a catalyst.

excess of I_2 would contaminate the products, and in the TEMPO-bleach protocol introduced by Anelli et al. CH_2Cl_2 usually was used as a biphasic system[4c] and chlorinated byproducts could be formed.[9] After screening several terminal oxidants listed in Table 1, we found $[dibmin]^+[BF_4]^-$ to be suitable for the reaction conducted in water, which based on the following reasons: (a) readily dissolving in water due to its ion-type structure; (b) acting as a role of phase transfer catalyst (PTC) to some extent to facilitate substrate dissolving in water; (c) most part of the oxidant, which was reduced easily precipitated out from water and recovered by filtration after the products extracted by Et_2O (the oxidant can be reoxidized by peracetic acid). The ion-supported TEMPO catalyst **4** remained in filtrate, which could be reused for next run after reloading the substrates and the oxidant $[dibmin]^+[BF_4]^-$.

Next, we examined the oxidation of a variety of primary and secondary alcohols in the presence of 5 mol% of ion-supported TEMPO (**4**, **6** or **7**) catalysts employing 1.2 mol equiv of $[dibmin]^+[BF_4]^-$ as a terminal oxidant. Under these conditions, of all most alcohols were quantitatively oxidized to carbonyl compounds within 330 min in good to excellent yields (Table 2). Benzylic primary alcohols (Table 2, entries 1–4 and 6) gave excellent yields of the corresponding aldehydes in very short reaction times (6–40 min) without any noticeable overoxidation to the carboxylic acids. This methodology is mild and compatible with several functional groups other than the hydroxyl group. For example, the ester linkage of ethyl 4-(hydroxymethyl)benzoate (Table 2, entry 6) remained intact. Cinnamyl alcohol (Table 2, entry 5) was oxidized to the corresponding aldehyde in 97% yield and no double-bond addition product was found. For the oxidation of benzylic secondary alcohols (Table 2, entries 12–15), the reaction afforded excellent yields but required 15–120 min for completion. The oxidation was relatively slow for the aliphatic primary and secondary alcohols (Table 2, entries 7–11), but the good yields could be obtained by extending reaction times. Notably, from the results, as expected, obtained in experiment, the catalytic activity for the catalyst **4** is the same as that for catalyst **6** (Table 2, entries 2, 5 and 13). The symmetric catalyst **7** gives the same yields as catalyst **4** or **6** in almost half reaction times and exhibits catalytic activities two times greater than catalyst **4** or **6** alone under similar conditions (Table 2, entries 5, 7–9 and 11), which implies this ion-supported catalyst with higher loading capacity would be more economic and potential in organic synthesis.

Table 2. Oxidation of alcohols catalyzed by ion-supported TEMPO catalysts (**4**, **6** or **7**) using $[dibmim]^+[BF_4]^-$ as terminal oxidant in water



Entry	Substrate	Product	Catalyst	Time (min)	Yield (%)[a]
1			**4**	6	97[b]
2			**4**	6	98
			6	6	98
3			**4**	15	97
4			**4**	10	97[b]
5			**4**	60	98
			6	60	97
			7	20	98
6			**4**	40	90
7			**4**	240	86
			7	90	85
8			**4**	240	95[b]
			7	120	93
9			**4**	330	85[b]
			7	180	88
10			**4**	300	86
11			**4**	300	80
			7	120	78
12			**4**	120	90[b]
13			**4**	30	99
			6	30	98
14			**4**	30	98
15			**4**	15	99

[a] Isolated yields after chromatographic purification unless otherwise noted.
[b] Yields were determined by GC.

To examine whether the catalytic activity of ion-supported TEMPO **6** decreases in recycling we compared it with the catalyst **4** under the same conditions described above using 4-methoxybenzyl alcohol as a substrate. The results are listed in Table 3. It was found that almost constant yields were obtained in five subsequent runs for both catalysts. No induction period was observed upon recycling of catalysts **4** and **6**.[4a] It suggested that the ester linkage of catalyst **6** probably was stable in reaction processes.

Table 3. Recyclability of ion-supported TEMPO catalysts **4** and **6** in the oxidation of 4-methoxylbenzyl alcohol

Catalyst	Cycle (yield %)[a]				
	1	2	3	4	5
4	98	97	96	98	97
6	98	96	98	97	94

[a] Reaction time 7 min.

3. Conclusion

In conclusion, we have successfully developed three ion-supported TEMPO catalysts and examined their catalytic activities. These low molecular weight catalysts displayed the same selectivities and activities as those of free TEMPO. The symmetric catalyst **7** noticeably increased the rate of oxidation of alcohols. Their combination with an ion-supported oxidant $[dibmin]^+[BF_4]^-$ afforded an easy workup and environmentally benign catalyst system for mild and selective oxidation of primary and secondary alcohols to carbonyl compounds. Both catalysts and oxidant could be recovered and recycled, and almost no waste was produced.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were determined in $CDCl_3$ or DMSO-d_6 on a Bruker 400 MHz spectrometer with TMS as the internal standard. IR spectra were recorded on a Bruker Vector-22 infrared spectrometer. C, H, N were analyzed on a Carlo Erba 1110 elemental analyzer. GC–MS analyses were performed on a Hewlett-Packard 5973 instrument (column: HP-5 30 m×0.25 mm×0.25 mm). All melting points were uncorrected. The columns were handpacked with silica gel H60 (~400). Reactions were carried out under atmosphere.

4.2. Synthesis of catalysts (4, 6, and 7)

The bromide, chloride, and tetrafluoroborate salts of ion-supported TEMPO were prepared by modification of published literature procedures.[22]

4.2.1. 4-(2,2,6,6-Tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide. To a solution of 4-hydroxy-TEMPO (2.58 g, 0.015 mol) in anhydrous acetone (25 mL) was added NaH (0.6 g, 0.015 mol) and the resulting slurry stirred for 10 min at room temperature. 1,4-Dibromobutane (4.86 g, 0.0225 mol) was then added and stirred for 3 h at room temperature. The acetone was removed under reduced pressure and water (30 mL) was added to dissolve the solid. The aqueous layer was then extracted with methylene chloride (15 mL×3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to a small volume. The resulting concentrated solution was separated by flash chromatography (10:1, petroleum/ethyl acetate) to obtain red oil 1.15 g (25%); ^1H NMR ($CDCl_3$, ppm): $\delta=1.17$ (s, 6H), 1.23 (s, 6H), 1.47 (t, $^3J(H,H)=11.6$ Hz, 2H), 1.68–1.73 (m, 2H), 1.90–1.96 (m, 4H), 3.42–3.47 (m, 4H), 3.50–3.57 (m, 1H); ^{13}C NMR ($CDCl_3$, ppm): $\delta=20.8$, 28.6, 29.7, 31.7, 33.8, 44.4, 59.7, 67.0, 70.4; IR (KBr): $\nu=2973$, 2937, 1459, 1376, 1363, 1245, 1177, 1104 cm^{-1}; MS (ESI): *m/z* (%): 306 (23.0) $[M^+]$, 308 (21.6) $[M^++2]$, 135 (93.2) $[C_4H_8Br^+]$, 137 (92.1) $[C_4H_8Br^++2]$, 55 (100.0) $[C_4H_7^+]$. Anal. Calcd for $C_{13}H_{25}BrNO_2$: C 50.82, H 8.20, N 4.56. Found: C 50.82, H 8.25, N 4.19.

4.2.2. 1-Methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium bromide. Under stirring, 0.922 g (3 mmol) of 4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide was slowly added to a solution of 0.295 g (3.6 mmol) of 1-methylimidazole in 1 mL of acetonitrile. The mixture was stirred for 6 h at 60 °C. After cooling to room temperature, 5 mL ether was added to the mixture causing precipitation of 1-methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium bromide as a red solid. This solid was recovered by filtration and washed with ether twice. The yield was 1.13 g (97%). Mp: 71–73 °C; ^1H NMR (DMSO-d_6, ppm): $\delta=1.03$ (s, 6H), 1.07 (s, 6H), 1.22–1.24 (m, 2H), 1.42–1.47 (m, 2H), 1.78–1.82 (m, 4H), 3.40 (t, $^3J(H,H)=6.4$ Hz, 2H), 3.49–3.54 (m, 1H), 3.86 (s, 3H), 4.19 (t, $^3J(H,H)=7.2$ Hz, 2H), 7.74 (s, 1H), 7.80 (s, 1H), 9.19 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): $\delta=20.9$, 26.6, 27.1, 32.8, 36.2, 45.0, 49.0, 58.3, 66.8, 70.4, 122.6, 124.0, 136.9; IR (KBr): $\nu=3087$, 2974, 2938, 1632, 1572, 1463, 1363, 1171, 1097 cm^{-1}; MS (ESI): *m/z* (%): 309 (8.5) $[M^+-Br^-]$, 124 (100.0) $[C_9H_{16}^+]$, 123 (66.4) $[C_7H_{15}^+]$, 81 (59.8) $[C_4H_5N_2^+]$, 55 (65.8) $[C_3H_5N^+]$, 42 (53.6) $[C_2H_4N^+]$. Anal. Calcd for $C_{17}H_{31}BrN_3O_2$: C 52.44, H 8.03, N 10.79. Found: C 52.09, H 8.09, N 10.98.

4.2.3. 1-Methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium tetrafluoroborate. The 1-methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)-butyl)imidazolium bromide obtained above 1.17 g (3 mmol) was added to a suspension of $NaBF_4$ (0.495 g, 4.5 mmol) in acetone (5 mL). The mixture was then stirred under the refluxing for 72 h. The sodium bromide precipitate was removed by filtration and the filtrate concentrated by rotary evaporation. The yield was 1.02 g (86%), red viscous oil; ^1H NMR (DMSO-d_6, ppm): $\delta=1.05$ (s, 6H), 1.08 (s, 6H), 1.25 (t, $^3J(H,H)=10.8$ Hz, 2H), 1.43–1.47 (m, 2H), 1.81–1.87 (m, 4H), 3.41 (t, $^3J(H,H)=6.4$ Hz, 2H), 3.50–3.55 (m, 1H), 3.85 (s, 3H), 4.18 (t, $^3J(H,H)=7.2$ Hz, 2H), 7.68 (s, 1H), 7.74 (s, 1H), 9.06 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): $\delta=20.8$, 26.6, 27.1, 32.7, 36.1, 44.9, 49.1, 58.5, 66.9, 70.3, 122.6, 124.0, 136.9; IR (KBr): $\nu=3159$, 2937, 2938, 1575, 1465, 1364, 1170, 1060 cm^{-1}; MS (ESI): *m/z* (%): 309 (1.0) $[M^+-BF_4^-]$, 137 (78.2) $[C_8H_{13}N_2^+]$, 83 (100.0) $[C_4H_7N_2^+]$, 55 (70.2) $[C_3H_5N^+]$, 42 (99.0) $[C_2H_4N^+]$.

Anal. Calcd for $C_{17}H_{31}BF_4N_3O_2$: C 51.53, H 7.89, N 10.60. Found: C 51.15, H 7.96, N 10.62.

4.2.4. 1,3-Bis(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl)imidazolium tetrafluoroborate. To a suspension of 0.245 g (3.6 mmol) of imidazole and 0.7 g potassium carbonate in acetone (10 mL) was added 1.84 g (6 mmol) of 4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide, and the mixture was stirred under the refluxing for 48 h. And then 0.396 g (3.6 mmol) $NaBF_4$ was added to the mixture to continue stirring for 72 h. The sodium bromide precipitate was removed by filtration and the filtrate concentrated by rotary evaporation. The yield was 1.50 g (82%), red viscous oil; ^{1}H NMR (DMSO-d_6, ppm): δ=1.04 (s, 12H), 1.07 (s, 12H), 1.22–1.26 (m, 4H), 1.37–1.42 (m, 4H), 1.70–1.76 (m, 4H), 1.82–1.86 (m, 4H), 3.37 (t, ^3J(H,H)=6.4 Hz, 4H), 3.48–3.52 (m, 2H), 3.96 (t, ^3J(H,H)=7.2 Hz, 4H), 7.61 (s, 2H), 8.96 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): δ=20.9, 27.0, 28.1, 30.0, 32.5, 32.8, 45.0, 46.2, 56.2, 58.3, 67.0, 68.9, 70.3, 119.6, 129.1, 137.6; IR (KBr): ν=2973, 2935, 2871, 1510, 1464, 1363, 1147, 1108 cm^{-1}; MS (ESI): *m/z* (%): 141 (43.2) [$C_9H_{19}N^+$], 124 (100.0) [$C_9H_{16}^+$]. Anal. Calcd for $C_{29}H_{53}BF_4N_4O_4$: C 57.24, H 8.78, N 9.21. Found: C 56.95, H 8.96, N 9.52.

4.2.5. 2,2,6,6-Tetramethyl-1-oxyl-4-piperidinyl 2-chloroacetate. To a solution of 4.3 g (0.025 mol) 4-hydroxy-TEMPO and 3.11 g (0.0275 mol) 2-chloroacetyl chloride in dichloromethane (30 mL) was slowly added 2.18 g (0.0275 mol) of pyridine under cooling, and the mixture was standing over night. The precipitate was removed by filtration and the filtrate was washed with water (30 mL), 10% $NaHCO_3$, then 2 mol dilute HCl and finally water (30 mL). The solution was dried over Na_2SO_4 and concentrated under vacuum to give red solid 4.98 g (80%). Mp: 49–51 °C; ^{1}H NMR ($CDCl_3$, ppm): δ=1.22 (s, 6H), 1.25 (s, 6H), 1.68 (t, ^3J(H,H)=11.6 Hz, 2H), 1.94–1.98 (m, 2H), 4.02 (s, 2H), 5.11–5.16 (m, 1H); ^{13}C NMR ($CDCl_3$, ppm): δ=20.4, 31.8, 41.0, 43.5, 59.2, 69.1, 166.8; IR (KBr): ν=2978, 2954, 1753, 1464, 1319, 1177, 1136 cm^{-1}; MS (ESI): *m/z* (%): 248 (14.5) [M^+], 250 (5.2) [M^++2], 124 (53.9) [$C_9H_{16}^+$], 109 (100), 41 (82.3). Anal. Calcd for $C_{11}H_{19}ClNO_3$: C 53.12, H 7.70, N 5.63. Found: C 52.99, H 7.73, N 5.54.

4.2.6. 1-Methyl-3-(2-oxo-2-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)ethyl)imidazolium chloride. (This procedure is similar to the preparation of bromide above). Mp: 225–227 °C; ^{1}H NMR (DMSO-d_6, ppm): δ=1.08 (s, 6H), 1.11 (s, 6H), 1.51 (t, ^3J(H,H)=11.6 Hz, 2H), 1.88–1.94 (m, 2H), 3.92 (s, 3H), 5.02–5.07 (m, 1H), 5.28 (s, 2H), 7.77 (s, 2H), 9.22 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): δ=20.7, 32.5, 36.3, 43.8, 49.9, 58.4, 69.3, 123.7, 124.1, 138.1, 166.9; IR (KBr): ν=2977, 1747, 1633, 1464, 1223, 1177 cm^{-1}; MS (ESI): *m/z* (%): 124 (34.3) [$C_6H_8N_2O^+$], 82 (100.0) [$C_4H_6N_2^+$], 56 (85.1) [$C_2H_4N_2^+$], 55 (91.2) [$C_4H_7^+$], 42 (84.2) [$C_2H_4N^+$]. Anal. Calcd for $C_{15}H_{25}ClN_3O_3$: C 54.46, H 7.62, N 12.70. Found: C 54.44, H 7.75, N 12.61.

4.2.7. 1-Methyl-3-(2-oxo-2-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)ethyl)imidazolium tetrafluoroborate. (This procedure is similar to the preparation of tetrafluoroborate above). Red oil; ^{1}H NMR (DMSO-d_6, ppm): δ=1.15 (s, 6H), 1.24 (s, 6H), 1.53 (t, ^3J(H,H)=11.2 Hz, 2H), 1.90–1.94 (m, 2H), 3.90 (s, 3H), 5.02–5.08 (m, 1H), 5.21 (s, 2H), 7.71 (s, 2H), 9.05 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm): δ=20.7, 32.3, 36.3, 43.6, 49.9, 58.6, 69.3, 1237, 124.1, 138.1, 166.8; IR (KBr): ν=2978, 2940, 1753, 1580, 1467, 1225, 1179, 1061 cm^{-1}; MS (ESI): *m/z* (%): 98 (68.2) [$C_5H_8NO^+$], 82 (46.2) [$C_4H_6N_2^+$], 55 (94.3) [$C_4H_7^+$], 41 (100.0) [$C_2H_3N^+$]. Anal. Calcd for $C_{15}H_{25}BF_4N_3O_3$: C 47.14, H 6.59, N 10.99. Found: C 46.86, H 6.76, N 10.63.

4.3. General procedure for alcohol oxidations

[dibmim]$^+$[BF_4]$^-$ (353 mg, 0.6 mmol) was added to a solution of alcohol (0.5 mmol) in 1.5 g of water containing 5% mmol of ion-supported TEMPO. The reaction mixture was stirred at 30 °C for a given time. The mixture was extracted with ether (3×8 mL) and concentrated under reduced pressure. The filtrate could be reused for next run after the oxidant in reduced form was removed by filtration. The product was purified by flash column chromatography using petroleum ether and Et_2O as eluent. All products were commercially available and identified by comparison of the isolated products with authentic samples.

4.3.1. Benzaldehyde. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ= 7.52–7.56 (m, 2H; Ar-H), 7.62–7.65 (m, 1H; Ar-H), 7.88–7.90 (m, 2H; Ar-H), 10.03 (s, 1H; CHO); IR (neat): ν=1703 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 106 (100) [M^+], 105 (94) [M^+−H], 77 (92) [$C_6H_5^+$].

4.3.2. 4-Methoxybenzaldehyde. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ=3.90 (s, 3H; CH_3), 7.01 (d, ^3J(H,H)=7.6 Hz, 2H; Ar-H), 7.85 (d, ^3J(H,H)=7.6 Hz, 2H; Ar-H), 9.89 (s, 1H; CHO); IR (neat): ν=1685 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 136 (76) [M^+], 135 (100) [M^+−H].

4.3.3. 4-Chlorobenzaldehyde. Mp: 46–47 °C; ^{1}H NMR ($CDCl_3$, ppm): δ=7.53 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H), 7.83 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H), 9.99 (s, 1H; CHO); IR (KBr): ν=1702 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 139 (100) [M^+], 141 (33) [M^++2].

4.3.4. Furaldehyde. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ= 6.61–6.63 (m, 1H), 7.27–7.30 (m, 1H), 7.70–7.71 (m, 1H), 9.67 (s, 1H; CHO); IR (neat): ν=1675 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 96 (100) [M^+], 95 (94) [M^+−H], 39 (58) [$C_3H_3^+$].

4.3.5. Cinnamaldehyde. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ= 6.73 (dd, ^3J(H,H)=8.0, 15.6 Hz, 1H; CH), 7.44–7.45 (m, 3H; Ar-H), 7.49 (d, ^3J(H,H)=15.6 Hz, 1H; CH), 7.56–7.58 (m, 2H; Ar-H), 9.71 (d, ^3J(H,H)=8.0 Hz, 1H; CH); IR (neat): ν=1679 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 132 (73) [M^+], 131 (100) [M^+−H], 103 (56) [$C_8H_7^+$].

4.3.6. Ethyl 4-formylbenzoate. Mp: 156–158 °C; ^{1}H NMR ($CDCl_3$, ppm): δ=1.43 (t, ^3J(H,H)=6.4 Hz, 3H; CH_3), 4.42 (q, ^3J(H,H)=6.4 Hz, 2H; CH_2), 7.96 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H), 8.21 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H), 10.11 (s, 1H; CHO); IR (KBr): ν=3058, 2981, 2924, 1711, 1274, 1102, 733 cm^{-1}; MS (70 eV): *m/z* (%): 178 (3.3) [M^+], 149 (100) [$C_9H_9O_2^+$].

4.3.7. 3-Phenylpropanal. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ= 2.77 (t, ^3J(H,H)=7.2 Hz, 2H; CH_2), 2.95 (t, ^3J(H,H)= 7.2 Hz, 2H; CH_2), 7.18–7.22 (m, 3H; Ar-H), 7.27–7.31 (m, 2H; Ar-H), 9.80 (s, 1H; CHO); IR (film): ν=3029, 2928, 2826, 1726, 1497, 1454, 747, 701 cm^{-1}; MS (70 eV): *m/z* (%): 134 (58.0) [M^+], 92 (75.3) [$C_7H_8^+$], 91 (100.0) [$C_7H_7^+$].

4.3.8. Hexanal. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ=0.93 (t, ^3J(H,H)=7.2 Hz, 3H; CH_3), 1.27–1.36 (m, 4H; CH_2), 1.51–1.58 (m, 2H; CH_2), 2.42 (t, ^3J(H,H)=7.2 Hz, 2H; CH_2), 9.77 (s, 1H; CHO); IR (film): ν=2960, 2932, 1718, 1460 cm^{-1}; MS (70 eV): *m/z* (%): 56 (82.1) [$C_4H_8^+$], 44 (100.0) [$C_2H_4O^+$].

4.3.9. Hexan-2-one. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ=0.91 (t, ^3J(H,H)=7.2 Hz, 3H; CH_3), 1.27–1.36 (m, 2H; CH_2), 1.52–1.60 (m, 2H; CH_2), 2.14 (s, 3H; CH_3), 2.43 (t, ^3J(H,H)=7.2 Hz, 2H; CH_2); IR (film): ν=2962, 2936, 1718, 1360, 1169 cm^{-1}; MS (70 eV): *m/z* (%): 100 (7.8) [M^+], 58 (49.1) [$C_4H_{10}^+$], 43 (100.0) [$C_2H_3O^+$].

4.3.10. 4-Hydroxycyclohexanone. Oil; ^{1}H NMR ($CDCl_3$, ppm): δ=1.95–2.01 (m, 2H), 2.03–2.08 (m, 2H), 2.28–2.37 (m, 2H), 2.58–2.65 (m, 2H), 3.80 (s, 1H), 4.19–4.23 (m, 1H); IR (KBr): ν=3386 (OH), 1707 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 114 (90.0) [M^+], 57 (78.4) [$C_3H_5O^+$], 55 (100.0) [$C_3H_3O^+$].

4.3.11. 4-Methylcyclohexanone. ^{1}H NMR ($CDCl_3$, ppm): δ=1.02 (d, ^3J(H,H)=6.8 Hz, 3H; CH_3), 1.37–1.48 (m, 2H), 1.86–1.94 (m, 1H; CH), 1.98–2.02 (m, 2H), 2.34–2.38 (m, 4H); IR (neat): ν=1714 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 112 (43) [M^+], 55 (100) [$C_3H_3O^+$].

4.3.12. Acetophenone. ^{1}H NMR ($CDCl_3$, ppm): δ=2.59 (s, 3H; CH_3), 7.43–7.47 (m, 2H; Ar-H), 7.54–7.57 (m, 1H; Ar-H), 7.95 (d, ^3J(H,H)=8.8 Hz, 2H; Ar-H); IR (neat): ν= 1686 cm^{-1} (C=O); MS *m/z* 120 (M^+). MS (70 eV): *m/z* (%): 120 (25) [M^+], 105 (100) [$C_7H_5O^+$], 77 (73) [$C_6H_5^+$].

4.3.13. 4-Methoxyacetophenone. Mp: 37–39°C; ^{1}H NMR ($CDCl_3$, ppm): δ=2.56 (s, 3H; CH_3), 3.87 (s, 3H; CH_3), 6.94 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H), 7.94 (d, ^3J(H,H)= 8.4 Hz, 2H; Ar-H); IR (KBr): ν=1677 cm^{-1} (C=O); MS *m/z* 150 (M^+). MS (70 eV): *m/z* (%): 150 (29) [M^+], 135 (100) [$C_8H_7O_2^+$].

4.3.14. 4-Bromoacetophone. Mp: 50–51°C; ^{1}H NMR ($CDCl_3$, ppm): δ=2.59 (s, 3H), 7.61 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H), 7.82 (d, ^3J(H,H)=8.4 Hz, 2H; Ar-H); IR (KBr): ν=1676 cm^{-1} (C=O); MS *m/z* 198 (M^+), 200 (M+2). MS (70 eV): *m/z* (%): 198 (29) [M^+], 200 (27) [M^++2], 183 (99) [$C_7H_4OBr^+$], 185 (100) [$C_7H_4OBr^+$].

4.3.15. 2-Hydroxy-1,2-diphenylethanone. Mp: 132–134 °C; ^{1}H NMR ($CDCl_3$, ppm): δ=4.56 (d, ^3J(H,H)= 6.0 Hz, 1H; OH), 5.96 (d, ^3J(H,H)=6.0 Hz, 1H; CH), 7.27–7.34 (m, 5H; Ar-H), 7.38–7.42 (m, 2H; Ar-H), 7.50–7.54 (m, 1H; Ar-H), 7.91–7.93 (m, 2H; Ar-H); IR (KBr): ν=3417 (OH), 1680 cm^{-1} (C=O); MS (70 eV): *m/z* (%): 212 (3) [M^+], 105 (100) [$C_7H_5O^+$].

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