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Aerobic Oxidation of Alcohols by Copper(I)/Benzoxazine Ligand/TEMPO under Mild and Base-Free Conditions[1]

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Abstract—A novel benzoxazine ligand with an imidazole moiety was synthesized. This ligand in combination with Cu(OTf) and TEMPO efficiently catalyzed aerobic oxidation of active primary alcohols and also showed good to excellent activity in the oxidation of secondary alcohols under mild and base-free conditions.

Keywords: benzoxazine ligand, copper(I) trifluoromethanesulfonate, aerobic oxidation, alcohols, TEMPO, base-free

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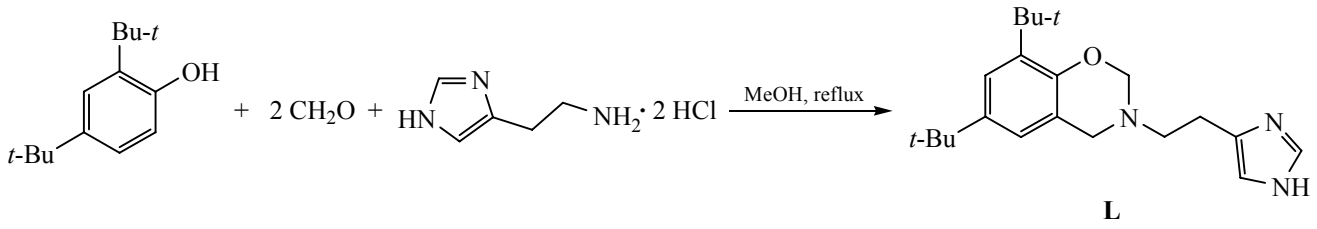
The oxidation of alcohols to the corresponding carbonyl compounds is one of the most important and ubiquitous reactions in organic synthesis [1–3]. In particular, this transformation is crucial for the synthesis of versatile intermediates for fragrances and food additives [4–6]. Classical oxidation methods require stoichiometric amounts of oxidants such as chromates [7–10], manganese dioxide [11–13], or selenium dioxide [14], which are sometimes toxic or hazardous. From the environmental and economic standpoints, molecular oxygen is an ideal oxidant which generates water as the only by-product in the oxidation process [15–20]. Catalytic oxidation systems employing molecular oxygen as a primary oxidant in combination with metal ions are particularly attractive [21–28]. Among the metals, copper is more attractive since it is an abundant metal on the earth's crust and copper ions are metal centers of enzymes such as galactose oxidase and tyrosinase [29, 30]. Thus, a series of copper-based catalysts or catalyst systems have been developed for the oxidation of alcohols to aldehydes and ketones with molecular oxygen. In 1984, Semmelhack and co-workers [31] were the first to report aerobic oxidation of benzylic and allylic alcohols with 10% CuCl/TEMPO in DMF as solvent. Aliphatic alcohols proved to be substantially less reactive and required 2 equiv of $CuCl_2$ to achieve good yields. Since then a number of copper/TEMPO catalyst systems have been proved to be highly efficient for the transformation of a broad range of alcohols to aldehydes and ketones [32–38]. It has been found that chelating nitrogen-containing ligands have beneficial effect on oxidation reactions. Notable examples include a (bipy)$CuBr_2$/TEMPO catalyst system that employs *t*-BuOK as a catalytic base in MeCN/H_2O as solvent [35–37], and (bipy)$Cu(OTf)_2$/TEMPO catalyst system [38]. Recently, more copper-based catalyst systems have been reported [39–49]. Stahl et al. [50] made a breakthrough in the development of copper/TEMPO systems. They disclosed a (bipy)Cu(I)/TEMPO/NMI catalyst system (NMI = *N*-methylimidazole) and found that replacement of Cu(II) by Cu(I) significantly enhanced the reaction rate. The catalytic system exhibits high rates and selectivity even with unactivated aliphatic alcohols. The other advantage of Stahl's catalyst system is the use of *N*-methylimidazole (NMI) instead of *t*-BuOK as a base. However, all the catalyst systems are complicatedly composed of four components: copper salt, ligand, base, and TEMPO, which is unfavorable for the isolation of the product.

Having been inspired by Stahl's catalyst system, we design a bidentate benzoxazine ligand containing an imidazole moiety which is expected to act both as ligand and base to simplify the catalytic system for the aerobic oxidation of alcohols. Encouragingly, the

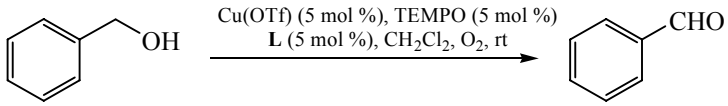
[1] The text was submitted by the authors in English.

Scheme 1.



L

Scheme 2.



benzoxazine ligand in conjugation with Cu(OTf) and TEMPO has shown excellent catalytic properties in the aerobic oxidation of various alcohols under mild and base-free conditions. Herein, we report the preparation of this novel ligand and the performance of the catalytic system based thereon for the oxidation of alcohols with molecular oxygen.

The benzoxazine ligand containing an imidazole moiety was readily synthesized by the Mannich condensation [51–53] of 2,4-di-*tert*-butylphenol with histamine dihydrochloride and aqueous formaldehyde in the presence of sodium hydroxide by heating for 40 h under reflux (Scheme 1). The structure of 6,8-di-*tert*-butyl-3-[2-(1*H*-imidazol-4-yl)ethyl]-3,4-dihydro-2*H*-1,3-benzoxazine was characterized by ^{1}H NMR, ^{13}C NMR and HRMS (ESI) data. Generally, the studies of benzoxazines are mainly focused on synthetic polymers which can be used as insulation materials, adhesives, glass fiber reinforce materials, coatings, phenolic resins, etc. [54–57]. Herein, the benzoxazine ring in combination with imidazole moiety will be used as a bidentate ligand in the copper-based catalytic system for the aerobic oxidation of alcohols.

Table 1. Effect of the composition of the Cu(OTf)/**L**/TEMPO catalytic system on the aerobic oxidation of benzyl alcohol[a]

Entry no.	Cu(OTf), mol %	TEMPO, mol %	**L**, mol %	Conversion,[b] %	Selectivity,[b] %
1	5	5	–	13.5	>99
2	5	–	5	16.2	>99
3	–	5	5	3.0	>99
4	5	5	5	99.4	>99

[a] Reaction conditions: benzyl alcohol, 1 mmol; CH_2Cl_2, 1 mL; room temperature, atmospheric oxygen pressure, reaction time 6.5 h. [b] The conversion and selectivity were determined by GLC (peak area normalization method).

Based on Stahl's catalytic system [50] bidentate ligand **L** in combination with Cu(OTf) and TEMPO [Cu(OTf)/**L**/TEMPO] was tested in the aerobic oxidation of benzyl alcohol as a model substrate (Scheme 2, Table 1). The reaction was carried out under atmospheric oxygen pressure at room temperature.

As shown in Table 1, the use of benzoxazine ligand **L** is essential. Only 13.5% of benzyl alcohol was converted to benzaldehyde in 6.5 h when no benzoxazine ligand was added (Table 1, no. 1). The presence of TEMPO and Cu(OTf) is crucial for the oxidation too. Only 16.2% of benzaldehyde was formed in 6.5 h without TEMPO (Table 1, no. 2), and almost no reaction was observed in the absence of Cu (OTf) (Table 1, no. 3). The results indicated that each component of the catalytic system is essential in the aerobic oxidation of benzyl alcohol. It is worth noting that, as we expected, the novel catalytic system is active without any extra base added. The complete conversion of benzyl alcohol into benzaldehyde is attained in 6.5 h in the absence of base (Table 1, no. 4).

Several other copper salts including copper(I) and copper(II) salts were also evaluated as catalyst precursors in the aerobic oxidation of benzyl alcohol. As shown in Table 2, Cu(OTf) worked well and showed the highest efficiency among all the copper salts tested, and the conversion of benzyl alcohol reached up to 90.2 % after 4 h (Table 2, no. 1). Both $Cu(OAc)_2 \cdot H_2O$ and CuCl led to less active catalysts

Table 2. Effect of the copper salt in the copper/**L**/TEMPO catalyst on the aerobic oxidation of benzyl alcohol[a]

Entry no.	Copper salt	Conversion,[b] %	Selectivity,[b] %
1	Cu(OTf)	90.2	>99
2	$Cu(OTf)_2$	86.1	>99
3	$Cu(OAc)_2 \cdot H_2O$	40.1	>99
4	CuCl	35.2	>99
5	$CuCl_2$	28.0	>99
6	$CuBr_2$	16.8	>99

[a] Reaction conditions: benzyl alcohol, 1 mmol; CH_2Cl_2, 1 mL; copper salt, 5 mol %; TEMPO, 5 mol %; **L**, 5 mol %; room temperature, atmospheric oxygen pressure, reaction time 4 h.
[b] The conversion and selectivity were determined by GLC (area normalization method).

Table 3. Effect of solvent on the copper(I)/**L**/TEMPO-catalyzed aerobic oxidation of benzyl alcohol[a]

Entry no.	Solvent (v/v)	Conversion,[b] %	Selectivity,[b] %
1	CH_3CN	11.7	>99
2	CH_3CN–H_2O (2/1)	10.5	>99
3	CH_2Cl_2	90.3	>99
4	CH_2Cl_2–H_2O (2/1)	47.5	>99
5	CH_2Cl_2–CH_3CN (1/1)	6.2	>99

[a] Reaction conditions: benzyl alcohol, 1 mmol; solvent, 1 mL; copper salt, 5 mol %; TEMPO, 5 mol %; **L**, 5 mol %; room temperature, atmospheric oxygen pressure, reaction time 4 h.
[b] The conversion and selectivity were determined by GLC (area normalization method).

with only 40.1% and 35.2% conversion after 4 h, respectively (Table 2, nos. 3, 4). Copper(II) chloride and bromide also produced unfavorable results with only 28.0% and 16.8% conversion, respectively (Table 2, nos. 5, 6). $Cu(OTf)_2$ afforded 86.0% conversion of benzyl alcohol in the same reaction time (Table 2, no. 2), i.e., it exhibited lower efficiency than Cu(OTf) as shown in Stahl's catalytic system [50]. The observed differences in the catalytic activity are likely to be related to the propensity for dissociation of the anion from the catalytic copper complex. Chloride, bromide, and acetate ions are more strongly coordinated to copper than $^-$OTf [37]. Consequently, the alcoholate enters the copper coordination sphere more easily when $^-$OTf is the counterion rather than other ions [50].

Based on a series of experiments dichloromethane was chosen as solvent. Initially, the reaction was run in anhydrous acetonitrile which was employed as solvent in Stahl's catalytic system [50]. However, only 11.7% conversion of benzyl alcohol was obtained in 4 h using that solvent (Table 3, no. 1). Then the oxidation reaction was performed in a 2 : 1 (v/v) acetonitrile/water mixture. However, no improvement was achieved (Table 3, no. 2). The poor results could be ascribed to the insolubility of the catalytic system in acetonitrile-based solvents. Finally, the reaction was run in dichloromethane where it proceeded smoothly. The conversion of benzyl alcohol reached 90.3% in 4 h (Table 3, no. 3). Furthermore, the addition of water or acetonitrile dramatically retarded the reaction (Table 3, nos. 4, 5).

The effect of temperature on the reaction was evaluated in the range from 15 to 35°C. Generally, the reaction rate increased with rise in temperature, and the selectivity for benzaldehyde remained constant.

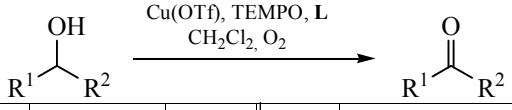
The catalytic system Cu(OTf)/**L**/TEMPO was then applied to the oxidation of various alcohols, including benzylic, allylic, heterocyclic, and aliphatic alcohols, and the results are summarized in Table 5. Various primary benzylic alcohols, including those bearing electron-withdrawing and electron-donating groups, were selectively converted to the corresponding aromatic aldehydes in excellent yields. Slightly different times were required to complete the reaction with *para*-substituted substrates (Table 5, nos. 1–3, 6, 8), but the difference between the substrates with

Table 4. Effect of temperature on the copper(I)/**L**/TEMPO-catalyzed aerobic oxidation of benzyl alcohol[a]

Entry no.	Temperature, °C	Time, h	Conversion,[b] %	Selectivity,[b] %
1	15	9	>99	>99
2	20	8	>99	>99
3	25	7	>99	>99
4	30	3	>99	>99
5	35	2.5	>99	>99

[a] Reaction conditions: benzyl alcohol, 1 mmol; solvent, 1 mL; copper salt, 5 mol %; TEMPO, 5 mol %; **L**, 5 mol %; atmospheric oxygen pressure.
[b] The conversion and selectivity were determined by GLC (area normalization method).

Table 5. Aerobic oxidation of various alcohols to carbonyl compounds catalyzed by Cu(OTf)/**L**/TEMPO[a]



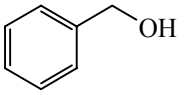
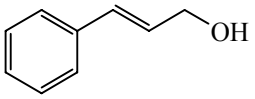
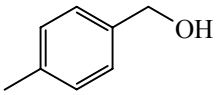
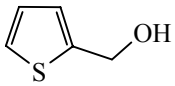
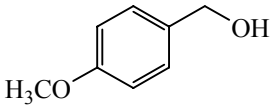
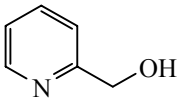
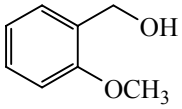
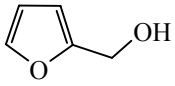
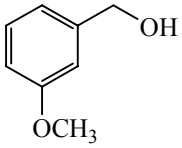
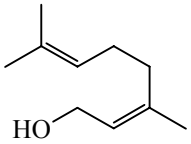
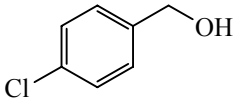
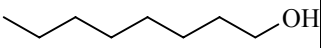
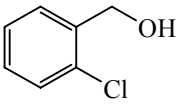
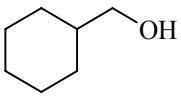
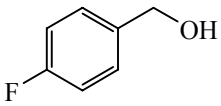
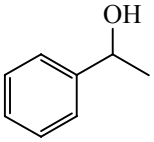
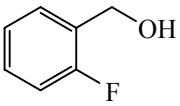
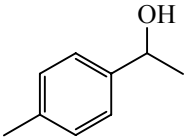
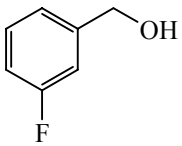
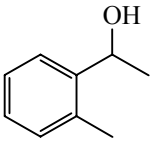
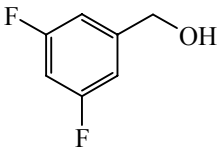
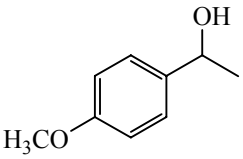
Entry no.	Substrate	Time, h	Conversion,[b] %	Selectivity,[b] %	Entry no.	Substrate	Time, h	Conversion,[b] %	Selectivity,[b] %
1[c]		7	>99 (92)	>99	12		9	>99 (91)	>99
2		6.5	>99	>99	13		8	>97 (89)	>99
3		4	>99 (86)	>99	14		4	30.1	>99
4		33	>98	>99	15		3.5	>99	>99
5		8	>99	>99	16		6	>99 (94)	>99
6		6.5	>99 (90)	>99	17		11	55.3	79.9
7		8	>99	>99	18		27.5	51.1	71.7
8		4.5	>99	>99	19		24	80.0	95.8
9		7	>99 (87)	>99	20		24	90.8	95.6
10		6.5	>99	>99	21		24	17.4	99
11		6	>99	>97	22		24	84.5	99

Table 5. (Contd.)

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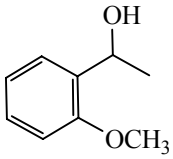
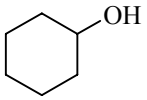
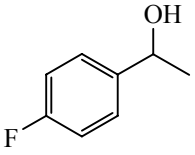
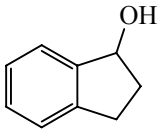
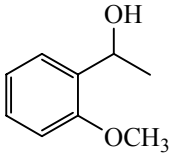
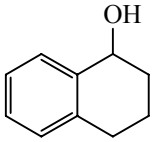
23		28.5	72.3	99	26		24	32.2	99
24		24	67.3	96.2	27		12	99.0	99
25		32.5	23.0	99.0	28		24	54.9	99

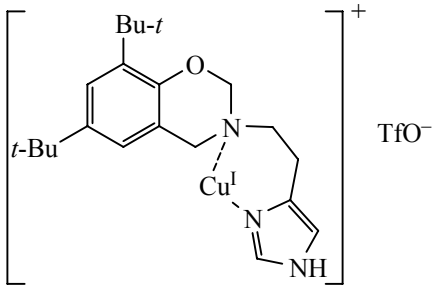
[a] Reaction conditions: alcohol, 1 mmol; atmospheric oxygen pressure. Primary alcohols: Cu(OTf), 5 mol %; TEMPO, 5 mol %; **L**, 4 mol %; CH_2Cl_2, 1 mL; room temperature. Secondary alcohols: Cu(OTf), 5 mol %; TEMPO, 5 mol %; **L**, 5 mol %; CH_2Cl_2, 2 mL; temperature 40°C. [b] The conversion and selectivity were determined by GLC (area normalization method); the isolated yields are given in parentheses; all products were identified by ^{1}H NMR. [c] The amount of benzyl alcohol was 40 mmol.

electron-withdrawing and electron-donating groups was not very obvious. This means that the electronic effect is not the main factor in the reaction. In contrast, the position of the substituent on the benzene ring appreciably affects the reactivity of benzylic alcohols. *ortho*-Substituted benzyl alcohols showed poor reactivity compared to *meta*- and *para*-substituted analogs due to steric hindrance (Table 5, nos. 3–5). The proposed catalytic system also showed good efficiency in the oxidation of some heterocyclic substrates, and good to excellent yields of the corresponding aldehydes were obtained under the optimal reaction conditions (Table 5, nos, 13, 15). However, primary alcohol bearing vicinal chelating group [50] like pyridin-2-ylmethanol proved to be less reactive, and the substrate conversion was incomplete even under increased loadings of the catalytic components, or/and extended reaction time, or/and elevated temperature (Table 5, no. 14). Allylic alcohols like cinnamyl alcohol and geraniol were completely converted into the corresponding aldehydes in 9 and 6 h, respectively, without enhancing reaction conditions (Table 5, nos. 12, 16). It is clear that the aerobic oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds is fast and efficient. However, aliphatic alcohols were still less reactive than benzylic or allylic alcohols resulting in lower conversions and yields, as observed with other copper-based catalytic systems [32, 34, 36, 37, 50]. For 1-octyl alcohol and cyclohexylmethanol, only ~50% conversion and less than 80% selectivity were observed even under prolonged reaction time or/and increased amounts of the catalyst components (Table 5, nos. 17, 18). The low reactivity of aliphatic alcohols can be attributed to the instability of TEMPO in the presence of aliphatic aldehydes and oxygen [31]. The major reason for the reduced selectivity is aldol condensation reaction, which is inferred from the results of analysis of the reaction mixture. It is very important to note that this system is also effective in the aerobic oxidations of secondary benzylic alcohols which are poor substrates for some copper-based catalyst systems [22, 31, 36, 37, 50, 58, 59]. Various secondary benzylic alcohols, including those bearing electron-withdrawing and electron-donating groups, were effectively and selectively converted to the corresponding ketones under relatively higher loadings of benzoxazine ligand (5 mol %) and higher reaction temperature (40°C) (Table 5, nos. 19, 20, 22–24). 1-(2-Methylphenyl) ethanol with an *ortho* substituent showed poor reactivity compared to those with *meta* and *para* substituents due to steric hindrance (Table 5, no. 21). 1-Hydroxyindan was completely converted into indan-1-one in 12 h. However, only 54.9% conversation was

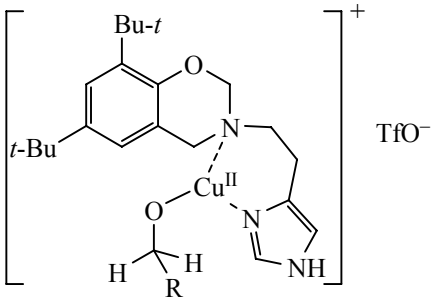
attained in the case of 1,2,3,4-tetrahydronaphthalen-1-ol even after extending the reaction time to 24 h. Secondary aliphatic alcohols showed poor reactivity compared to secondary benzylic alcohols (Table 5, nos. 25, 26). In general, the benzoxazine ligand-mediated catalytic system has broad applicability in the aerobic oxidations of both primary and secondary alcohols under base-free conditions.

To demonstrate scalability of this catalytic system, the reaction with benzyl alcohol as substrate was carried out on a multigram scale. The same results were obtained when the amount of benzyl alcohol was increased to 40 mmol (Table 5, no. 1).

It is difficult to propose a detailed mechanism for the novel catalytic system at this stage. However, we believe that initially Cu(I)–benzoxazine complex **A** is generated *in situ* via coordination of benzoxazine ligand **L** to Cu(OTf). As noted above, the catalytic activity of the catalytic system is related to steric hindrance of the substrate, which is consistent with the results observed in the (bipy)Cu/TEMPO-catalyzed oxidation of alcohols [35, 36, 50]. Taking into account these data, as well as the mechanisms for (bipy)Cu/TEMPO-catalyzed oxidation of alcohols described in [35, 36], especially the mechanism for (bipy)Cu(OTf)/TEMPO-catalyzed oxidation of alcohols recently proposed by Stahl [60], copper(II) alkoxide complex **B** might be formed in the catalytic cycle. Once the complex is formed, a hydrogen atom is abstracted from the Cu(II) alkoxide by TEMPO to give the aldehyde [60].



A



B

In conclusion, a novel benzoxazine ligand with an imidazole moiety has been synthesized. This ligand in combination with Cu(OTf) and TEMPO showed excellent performance in the oxidation of various alcohols to the corresponding carbonyl compounds under very mild base-free conditions. In all cases, benzylic and allylic alcohols were selectively oxidized to the corresponding aldehydes, and no over-oxidized products (carboxylic acids) were detected. The novel catalytic system not only offers the advantages of performing aerobic oxidation of active primary alcohols under mild and base-free conditions, but also has certain catalytic activity for the selective oxidation of secondary alcohols.

EXPERIMENTAL

2,4-Di-*tert*-butylphenol was purchased from Aldrich. Histamine hydrochloride was obtained from Shanghai Yuanye Bio-Technology Co., Ltd. Formaldehyde solution and sodium hydroxide were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. Alcohols were obtained from Alfa Aesar China (Tianjin) Co., Ltd. All the chemicals were used as received. Solvents were purified by standard methods and dried if necessary.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-P 400 spectrometer using TMS as internal standard. The mass spectra (ESI) were recorded on an LCQ Advanced high-resolution spectrometer. The reaction mixtures were analyzed on a Shandong Lunan Ruihong Gas Chromatograph (SP-6800A) equipped with a flame ionization detector and a SE-30 column (30 m × 0.5 mm); detector temperature 280°C, oven temperature 130–220°C (depending on the alcohol), carrier gas inlet pressure 0.05–0.07 MPa (depending on the alcohol), injection split ratio 10 : 1.

6,8-Di-*tert*-butyl-3-[2-(1*H*-imidazol-4-yl)ethyl]-3,4-dihydro-2*H*-1,3-benzoxazine (L). A solution of 2.40 g (60 mmol) of sodium hydroxide in 20 mL of MeOH was added dropwise to a solution of 6.19 g (30 mmol) of 2,4-di-*tert*-butylphenol, 5.52 g (30 mmol) of histamine dihydrochloride, and 5.00 mL (60 mmol) of aqueous formaldehyde in 60 mL MeOH. The mixture was heated for 40 h under reflux with vigorous stirring under atmospheric pressure, the

solvent was evaporated under reduced pressure, and the residue was extracted with ethyl acetate. The extract was dried over anhydrous sodium sulfate, the drying agent was filtered off, and the filtrate was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (*n*-hexane–ethyl acetate, 2 : 1 by volume) to obtain 6,8-di-*tert*-butyl-3-[2-(1*H*-imidazol-4-yl)ethyl]-3,4-dihydro-2*H*-1,3-benzoxazine as a white solid. Yield 2.15 g (21%), mp 201.2°C. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.27 s and 1.37 s (9H each, *t*-Bu), 2.71 t (2H, 4′-CH_2, J = 4 Hz), 2.90 t (2H, 3-CH_2, J = 6 Hz), 3.58 s (2H, 4-H), 3.90 s (2H, 2-H), 6.91 d and 7.19 d (1H each, 5-H, 7-H, J = 4 Hz), 7.53 s (1H, imidazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.16, 29.57, 31.60, 31.68, 34.13, 34.83, 49.30, 50.47, 61.11, 120.61, 123.04, 123.44, 133.91, 135.60, 140.61, 154.32. Mass spectrum: *m*/*z* 341.2553. $C_{21}H_{31}N_3O$. Calculated: *M* 341.2467.

Typical procedure for the oxidation of primary alcohols. A 5-mL two-necked, round-bottom flask equipped with a magnetic stirrer and an oxygen balloon was charged in succession with 0.0106 g (0.05 mmol) of Cu(OTf), 0.0078 g (0.05 mmol) of TEMPO, 0.0136 g (0.04 mmol) of benzoxazine ligand **L**, and 1 mL of methylene chloride. The corresponding alcohol, 1 mmol, was then added at 25°C under stirring, and oxygen from the balloon was introduced through a three-way valve. The progress of the reaction was monitored by GLC using a suitable column.

Typical procedure for the oxidation of secondary alcohols. A 5-mL two-necked, round-bottom flask equipped with a magnetic stirrer and an oxygen balloon was charged in succession with 0.0106 g (0.05 mmol) of Cu(OTf), 0.0078 g (0.05 mmol) of TEMPO, 0.0171 g (0.05 mmol) of benzoxazine ligand **L**, and 2 mL of methylene chloride. The corresponding alcohol, 1 mmol, was then added at 40°C under stirring, and oxygen from the balloon was introduced through a three-way valve. The progress of the reaction was monitored by GLC using a suitable column.

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