Vanadium-Catalyzed Green Oxidation of Benzylic Alcohols in Water under Air Atmosphere

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ABSTRACT

The oxidation of alcohols using catalytic amounts of metal complexes is highly attractive from the viewpoint of green chemistry principles. However, examples of metal complex-catalyzed oxidations of alcohols with O₂ using water as the solvent are still rare, and precious metals, high-pressure O₂ or air, and a stoichiometric amount of base are often required. In this study, it was found that an oxovanadium–4,4'-*t*-Bubpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) complex exhibited high catalytic activity in the oxidation of benzhydrols under an atmosphere of O₂ in water as the sole solvent. Interestingly, this catalytic oxidation method could be applied to the gram-scale aerobic oxidation of alcohols in water under the atmosphere.

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Introduction

The oxidation of alcohols to aldehydes and ketones is one of the most important synthetic transformations for the organic chemist with respect to the useful intermediates obtained for the preparation of more complex organic compounds.¹ Conventionally, stoichiometric amounts of heavy metals (e.g., chromium(VI)) are used as oxidants. Therefore, the oxidation of alcohols using catalytic amounts of metal complexes is a highly attractive prospect from the viewpoint of green chemistry principles,² in which the following reaction characteristics are desired: (1) the use of earth-abundant transition metals in terms of sustainability and cost; (2) use of molecular oxygen (O₂) as a terminal oxidant, where water is the only by-product; (3) use of water in place of organic solvents due to its low cost and inflammability, and great abundance.⁸ However, examples of metal complex-catalyzed oxidations of alcohols with O₂ using water as the solvent are still rare.⁹ Precious metals (e.g., Au, Ru, and Pd), high-pressure O₂ or air, and a stoichiometric amount of base are often required.

Vanadium is a relatively abundant element, ranking among the top 20 elements occurring in the earth's crust. The oxidative properties of pentavalent vanadium are well known.¹⁰ Recent studies have focused on the development of vanadium catalysts for the oxidation of alcohols with O₂;¹¹ nonetheless, no reports are known to exist of an efficient vanadium catalytic system for aerobic oxidation of alcohols using water as the only solvent under atmospheric conditions.

Recently, we have reported the aerobic oxidation of benzylic alcohols catalyzed by (VO)₄(hpic)₄ or VO(Hhpic)₂, which are synthesized from VOSO₄ and 3-hydroxypyridine-2-carboxylic acid (H₂hpic).^{12(a), (b)} Recyclability was observed in (VO)₄(hpic)₄, while VO(Hhpic)₂ was noted to have relatively high catalytic activity (Scheme 1).

Scheme 1 Oxidation of benzhydrol using VO(Hhpic)₂ or (VO)₄(hpic)₄

Opportunately, we also found that VO(Hhpic)₂ could also oxidize benzylamines to the corresponding imines with high selectivity using an ionic liquid solvent under an atmosphere of O₂ (0.1 MPa), also with good recyclability (Scheme 2).^{12(c)}

Scheme 2 Oxidation of benzylamine using recyclable vanadium catalyst VO(Hhpic)₂ in ionic liquid

Scheme 3 Oxidation of benzhydrol using heterotetranuclear complexes

Furthermore, the oxidation of alcohols with H₂O₂ using heterotetranuclear complexes bearing bipyridyl ligands in water as solvent was already reported (Scheme 3).^{12(d)}

Herein, we report the efficient oxidation of benzyl alcohol derivatives using an oxovanadium–2,2′-bipyridyl complex using water as the sole solvent under an atmosphere of O₂; the ligand 4,4′-di-*tert*-butyl-2,2′-bipyridyl (4,4′-*t*-Bubpy) provides the greatest yields of oxidation products.^{12(e)} Furthermore, this reaction system could also be used for gram-scale oxidation reactions under atmospheric pressure in air. To the best of our knowledge, this is the first report of an efficient catalytic system employing vanadium for the aerobic oxidation of alcohols using water as the only solvent under atmospheric conditions. We have also focused on using H₂O as safer and abundant.

Results and discussion

Firstly, to determine the most effective ligand for catalysis, as preliminary experimental, a series of H₂hpic derivatives were screened (Table 1, entries 1–5). It was found that the pyridine unit was essential for the useful catalytic activity of vanadium (entry 5). An examination of several pyridine derivatives revealed that the functional group identity on the pyridine unit affects reaction efficiency to some extent (entries 6–9). Next, the bidentate 2,2′-bipyridyl ligand consisting of two pyridine units was applied to this oxidation. In entry 11, the yield of the corresponding ketone was found to have increased compared with entry 5. More interestingly, an over-oxidation product (benzoic acid) was observed when 2,2′-bipyridyl was used (entry 10). These data suggest that a bidentate ligand is more efficient than monodentate ligand in the oxidation, and that the bipyridyl unit in particular appears to be the most effective for the oxidative activity of vanadium.

A number of oxovanadium compounds including VO(Hhpic)₂, previously identified as an oxidant with good catalytic activity (cf. Scheme 2), were examined in the oxidation of benzhydrol (**1a**) in water under an O₂ atmosphere (0.1 MPa) at 90 °C, and resulting products were identified by NMR. Unfortunately, VO(Hhpic)₂ and VOSO₄ were not effective under the reaction conditions (Table 2, entries 2, 3). Also, the addition of H₂hpic was found to be ineffective for the VOSO₄-catalyzed reaction (entry 4). In sharp contrast, when 4,4′-*t*-Bubpy was used as a

Table 1 Examination of ligand effects on vanadium-catalyzed oxidation

VO(Hhpic) ₂ , O ₂ (0.1 MPa) Ionic liquid, 120 °C, 6 h			VOSO ₄ (2 mol%), ligand (4 mol%) O ₂ (1.0 MPa) MeCN, 120 °C, 3 h		
Ph-CH ₂ -NH ₂		Ph-CH=N-Ph	Ph-CH ₂ -OH		Ph-C(=O)-H
Entry	Ligand	Yield (%) ^a	Entry	Ligand	Yield (%) ^a
1		48	7		38
2		12	8		49
3		7	9		7
4		5	10		17 (29)
5		40 (9)	11		55
6		55			

^a Determined by ¹H NMR. Yield of benzoic acid is shown in parentheses.

Table 2 Vanadium catalyst activities for oxidation of benzhydrol^a

Ph-CH(OH)-Ph 1a		catalyst (5 mol%), ligand (10 mol%) O ₂ (0.1 MPa) H ₂ O (0.5 mL), 90 °C		Ph-C(=O)-Ph 2a	
Entry	Catalyst	Ligand	Time (h)	Yield of 2a (%) ^b	
1	None	None	3	N.D.	
2	VOSO ₄	None	3	trace	
3	VO(Hhpic) ₂	None	3	N.D.	
4	VOSO ₄	H ₂ hpic	3	trace	
5	[VO(<i>t</i> -Bubpy) ₂] ₂ SO ₄	None	3	43	
6	VOSO ₄	4,4′- <i>t</i> -Bubpy	3	47	
7	VOSO ₄	4,4′-DCbpy	3	2	
8	VOSO ₄	6,6′-Mebpy	3	N.D.	
9	VOSO ₄	4,4′- <i>t</i> -Bubpy	6	83	
10	VOSO ₄	5,5′-Mebpy	6	76	
11	VOSO ₄	4,4′-Mebpy	6	33	
12	VOSO ₄	4,4′-MeObpy	6	19	
13	VOSO ₄	4,4′-Phbpy	6	trace	
14	VOSO ₄	Phen	6	22	
15	VOSO ₄	Bpy	6	17	

^a Reaction conditions: catalyst (0.005 mmol), ligand (0.01 mmol), **1a** (0.1 mmol), H₂O (0.5 mL), O₂ (0.1 MPa), 90 °C. ^b Determined by ¹H NMR. N.D.: Not detected. 4,4′-DCbpy: 2,2′-bipyridine-4,4′-dicarboxylic acid. 6,6′-Mebpy: 6,6′-dimethyl-2,2′-bipyridyl. 5,5′-Mebpy: 5,5′-dimethyl-2,2′-bipyridyl. 4,4′-Mebpy: 4,4′-dimethyl-2,2′-bipyridyl. 4,4′-MeObpy: 4,4′-dimethoxy-2,2′-bipyridyl. 4,4′-Phbpy: 4,4′-diphenyl-2,2′-bipyridyl. Phen: phenanthroline. Bpy: 2,2′-bipyridine.

ligand, the oxidation of **1a** proceeded successfully in moderate yield (entry 5). The addition of 4,4′-*t*-Bubpy was also effective

Table 3 Vanadium-catalyzed oxidation of benzhydrol derivatives under O₂ atmosphere in water^a

$\text{R}^1\text{CH(OH)R}^2 \xrightarrow[\text{H}_2\text{O (0.5 mL), 90 }^\circ\text{C}]{\text{VOSO}_4 \text{ (5 mol\%), ligand (10 mol\%)}, \text{O}_2 \text{ (0.1 MPa)}} \text{R}^1\text{C(=O)R}^2$					
Entry	R ¹	R ²	Time (h)	Yield of 2 (%) ^b	
1	Ph	Ph	1a 6	2a (87)	
2	4-MeOC ₆ H ₄	Ph	1b 8	2b 83	
3	4-BrC ₆ H ₄	Ph	1c 6	2c (84)	
4	4-NO ₂ C ₆ H ₄	Ph	1d 8	2d (83)	
5	4-MeC ₆ H ₄	4-MeC ₆ H ₄	1e 6	2e 86	
6	Ph	Me	3a 3	4a trace	

^a Reaction conditions: VOSO₄ (0.005 mmol), 4,4'-*t*-Bubpy (0.01 mmol), substrate (0.1 mmol), H₂O (0.5 mL), O₂ (0.1 MPa), 90 °C. ^b Determined by ¹H NMR. Isolated yields are shown in parentheses.

for the VOSO₄-catalyzed reaction (entry 6). A cursory examination of several bipyridyl derivatives in the oxidation reaction demonstrated that 4,4'-*t*-Bubpy was the most effective ligand (entries 7–15). Steric bulk around the ligand co-ordination site had varying effects on reaction efficiency; 6,6'-dimethyl-2,2'-bipyridyl (6,6'-Mebpy) was ineffective (entry 7), most likely because approach of the substrate to the central metal was inhibited by the functional groups blocking the metal site.

Oxidation of other substrates using 4,4'-*t*-Bubpy as a ligand was also investigated under an atmosphere of O₂ in water (Table 3). Benzhydrol derivatives (**1**) with an electron-donating or electron-withdrawing group could be oxidized to the corresponding carbonyl compounds in high yields (entries 1–5).

In the case of 1-phenylethanol (**3a**), however, the reaction proceeded ineffectively (Table 3, entry 6). After further optimization of the reaction conditions, it was noticed that addition of a catalytic amount of **1a** promoted the oxidation of the **3a**; acetophenone (**4a**) was obtained in this manner in 22% yield (Table 4, entry 1). Furthermore, using sat. MgSO₄(aq) and scaling up substrate loading from 0.1 mmol to 0.5 mmol

Table 4 Oxidation in the presence of benzhydrol additives^a

$\text{R}^1\text{CH(OH)Me} \xrightarrow[\text{H}_2\text{O (2.5 mL), 90 }^\circ\text{C}]{\text{VOSO}_4 \text{ (5 mol\%), 4,4'-}t\text{-Bubpy (10 mol\%)}, \text{MgSO}_4 \text{ (7.5 mmol), benzhydrols (10 mol\%)}, \text{O}_2 \text{ (0.1 MPa)}} \text{R}^1\text{C(=O)Me}$				
Entry	R	benzhydrols	Yield of 4 (%) ^b	
1 ^c	Ph	3a 1a	4a 22	
2	Ph	3a 1a	4a 67	
3 ^d	Ph	3a 1a	4a 72	
4 ^d	4-NO ₂ C ₆ H ₄	3d 1a	4d 27	
5 ^d	4-BrC ₆ H ₄	3c 1a	4c 51	
6	4-BrC ₆ H ₄	3c 1c	4c 82	
7	4-BrC ₆ H ₄	3c 1d	4c 92	
8	4-BrC ₆ H ₄	3c 1e	4c 44	

^a Reaction conditions: VOSO₄ (0.025 mmol), 4,4'-*t*-Bubpy (0.05 mmol), substrate (0.5 mmol), MgSO₄ (7.5 mmol), H₂O (2.5 mL), O₂ (0.1 MPa), 90 °C, 22 h. ^b Determined by ¹H NMR. ^c Substrate (0.1 mmol) in the absence of MgSO₄, reaction time: 6 h. ^d Substrate (1.0 mmol), MgSO₄ (15 mmol).

Table 5. Time-course change of oxidation of **1a**^a

$\text{PhCH(OH)Me} \xrightarrow[\text{H}_2\text{O (0.5 mL), 90 }^\circ\text{C}]{\text{VOSO}_4 \text{ (5 mol\%), 4,4'-}t\text{-Bubpy (10 mol\%)}, \text{1a (10 mol\%)}, \text{O}_2 \text{ (0.1 MPa)}} \text{PhC(=O)Me} + \text{PhCH(OH)Ph} + \text{PhC(=O)Ph}$					
Entry	Time (h)	Yield (%) ^b			
		3a	4a	1a	2a
1	0.5	88	1	67	13
2	2	83	3	6	42
3	4	81	6	N.D.	63
4	13	58	22	N.D.	63
5	23	44	31	N.D.	70

^a Reaction conditions: VOSO₄ (0.005 mmol), 4,4'-*t*-Bubpy (0.01 mmol), **1a** (0.01 mmol), H₂O (0.5 mL), substrate (0.1 mmol), O₂ (0.1 MPa), 90 °C. ^b Determined by ¹H NMR. N.D.: Not detected.

Table 6 Oxidation of benzyl alcohol derivatives under an O₂ atmosphere^a

$\text{R}^1\text{CH(OH)R}^2 \xrightarrow[\text{H}_2\text{O (2.5 mL), 90 }^\circ\text{C}]{\text{VOSO}_4 \text{ (5 mol\%), 4,4'-}t\text{-Bubpy (10 mol\%)}, \text{MgSO}_4 \text{ (7.5 mmol), 1d (10 mol\%)}, \text{O}_2 \text{ (0.1 MPa)}} \text{R}^1\text{C(=O)R}^2$					
Entry	R ¹	R ²	Time (h)	Yield of 4 (%) ^b	
1	4-MeOC ₆ H ₄	Me	3d 12	4d 54	
2	4-NO ₂ C ₆ H ₄	Me	3f 48	4f 75	
3	Ph	ⁿ Bu	3g 23	4g 86	
4	Ph	ⁱ Pr	3h 22	4h 55	
5	Ph	ⁱ Hex	3i 23	4i 77	
6	2-thienyl	Me	3j 40	4j 48	
7	Ph	H	3k 22	4k 24 (61)	
8	4-MeC ₆ H ₄	H	3l 22	4l 35 (26)	
9	4-MeOC ₆ H ₄	H	3m 22	4m 77 (23)	
10	4-BrC ₆ H ₄	H	3n 22	4n 65 (12)	
11	4-ClC ₆ H ₄	H	3o 22	4o 56 (22)	
12	4-NO ₂ C ₆ H ₄	H	3p 22	4p 43 (31)	

^a Reaction conditions: VOSO₄ (0.025 mmol), 4,4'-*t*-Bubpy (0.05 mmol), **1d** (0.05 mmol), H₂O (2.5 mL), MgSO₄ (7.5 mmol), substrate (0.5 mmol), O₂ (0.1 MPa), 90 °C. ^b Determined by ¹H NMR. Yield of carboxylic acids are shown in parentheses.

improved reaction efficiency and yield of the desired product (67%, entry 2). Further substrate scale-up increased the product yield only minimally (entry 3). For oxidation of other benzyl alcohols, the benzhydrol additive was less effective (entries 4, 5). Several benzhydrol derivatives were examined for the oxidation of *p*-bromo- α -methylbenzyl alcohol (**1h**), with oxidation proceeding in moderate to high yields. It was apparent that *p*-nitrobenzhydrol (**1d**) was most effective as an additive in the present oxidation system, with the corresponding ketone obtained in 92% yield (entry 7).

Next, the time-course of the vanadium-catalyzed oxidation of **3a** using catalytic **1a** as an additive was investigated in further

Scheme 4 Oxidation of **1a** under open-air conditions in water **Scheme 5** Gram-scale oxidation of **1a** under open-air conditions **Table 7** Oxidation of benzhydrol derivatives under open air-atmosphere^a

$\begin{array}{c} \text{OH} \\ \\ \text{R}^1-\text{C}-\text{R}^2 \\ \mathbf{1} \end{array} \xrightarrow[\text{H}_2\text{O (50 mL), 90 }^\circ\text{C, 96 h, open air}]{\text{VOSO}_4 \text{ (5 mol\%), 4,4'-t-Bubpy (10 mol\%), MgSO}_4 \text{ (150 mmol)}} \begin{array}{c} \text{O} \\ \\ \text{R}^1-\text{C}-\text{R}^2 \\ \mathbf{2} \end{array}$			
Entry	Substrate 1	Yield of 2 (%) ^b	
1		1b 2b	90
2		1c 2c	88
3		1d 2d	48 (67)
4		1e 2e	61
5		1f 2f	90
6		1g 2g	90
7		1h 2h	69
8		1i 2i	57

^a Reaction conditions: VOSO₄ (0.5 mmol), 4,4'-t-Bubpy (1 mmol), H₂O (50 mL), MgSO₄ (150 mmol), substrate (10 mmol), 90 °C, open-air atmosphere. ^b Isolated yield. ¹H NMR yields are shown in parentheses.

detail by ¹H NMR analysis. Over the reaction course, the yield of **4a** continued to increase with the complete consumption of **1a**, which was oxidized to **2a** (Table 5). The oxidation of **3a** using

Table 8 Oxidation of secondary benzyl alcohol derivatives under open-air atmosphere^a

Entry	Substrate 3	Yield of 4 (%) ^b	
1		3g 4g	83 (88)
2		3i 4i	81
3		3j 4j	85 (98)
4		3k 4k	92 (97)
5		3l 4l	80 (84)
6		3m 4m	70 (89)
7		3n 4n	(92)
8		3o 4o	83 (98)

^a Reaction conditions: VOSO₄ (0.5 mmol), 4,4'-t-Bubpy (1 mmol), **1d** (1 mmol), H₂O (50 mL), MgSO₄ (150 mmol), substrate (10 mmol), 90 °C, open-air atmosphere. ^b Isolated yield. ¹H NMR yields are shown in parentheses.

2a as an additive was also investigated, but the reaction proceeded inefficiently. Furthermore, oxidation of **3c** suggested that substituents on the aromatic ring of benzhydrol additives may affect the activity of the vanadium catalyst (See Table 4, entries 5–9).¹³

Oxidation of benzyl alcohol derivatives (**3**) was studied next using the optimized conditions (Table 6). Oxidation of secondary benzyl alcohols proceeded smoothly, with the corresponding ketones obtained in good to high yields (entries 1–6). Benzyl alcohols with electron-withdrawing groups required prolonged reaction times, giving the corresponding ketone in moderate yield (entry 2). This system could be applied to the oxidation of 1-(2-thienyl)ethanol (**3j**), a heterocyclic example; 2-acetylthiophene (**4n**) was obtained in 48% yield (entry 6).

We next applied our catalytic system to the oxidation of benzhydrol under an open-air atmosphere, the mildest possible condition in the oxidation reaction (Scheme 4). Interestingly, the oxidation proceeded successfully by prolonging the reaction time

Table 9 Effect of salts on the oxidation of **1a**^a

$ \begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{1a} \end{array} \xrightarrow[\text{H}_2\text{O, 90 }^\circ\text{C, open air}]{\text{VOSO}_4 \text{ (5 mol\%), 4,4'-}t\text{-Bubpy (10 mol\%)}} \begin{array}{c} \text{O} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{2a} \end{array} $			
Entry	Additive	Time (h)	Yield (%) ^b
1	MgSO ₄ (7.5 mmol)	48	24
2	MgSO ₄ (150 mmol)	48	42
3	NaCl (330 mmol)	48	(11)
4	MgSO ₄ (150 mmol)	96	94
5	Na ₂ SO ₄ (152 mmol)	96	(80)
6	(NH ₃) ₂ SO ₄ (150 mmol)	96	43
7	K ₂ SO ₄ (150 mmol)	96	73

^a Reaction conditions: VOSO₄ (0.5 mmol), 4,4'-*t*-Bubpy (1 mmol), H₂O (50 mL), additive, benzhydrol (10 mmol), 90 °C, open-air atmosphere. The amounts of additives were adjusted to be saturated in 90 °C. ^b Isolated yield. ¹H NMR yields are shown in parentheses.

to 48 h; the corresponding ketone was successfully obtained in 75% yield.

Gram-scale aerobic oxidation of benzhydrol was also examined (Scheme 5). The oxidation proceeded to yield benzophenone in moderate yield (57%). The addition of sat. MgSO₄ (aq) to the reaction mixture allowed for benzophenone to be obtained in a vastly improved yield (94%). Moreover, the oxidation was also proceeded efficiently, when the catalyst amount was reduced to 1 mol%.

From these results, gram-scale oxidations of benzhydrol derivatives under open-air conditions in sat. MgSO₄ (aq) were performed. Stirring under open-air condition in water, the corresponding ketones were obtained in moderate to high yields (Table 7).

Gram-scale oxidation of benzyl alcohol derivatives was also investigated. Secondary benzyl alcohols were oxidized successfully in water under open air conditions and the corresponding ketones were obtained in high yields (Table 8). The procedure could also be successfully applied to alcohols having long-chained alkyl groups.

The effects of additives were studied. VOSO₄ was soluble in water in our oxidation system; in contrast, the ligands and substrates were insoluble, and would float on the aqueous solution of vanadium. The complexation of vanadium with ligands began by heating the mixture, which melted the substrate; the vanadium complex was then able to solubilize in this organic phase. From these results, we presume that this oxidation proceeds in the organic layer composed of the substrate. To improve the efficiency of substrate contact with the vanadium complex, several salts were added to the reaction system; MgSO₄ was found to be the most effective additive for solubilization in the established reaction system (Table 9).¹³

A plausible reaction pathway is proposed in Figure 1.^{11c} Firstly, complex **A** is provided by the reaction of alcohol and catalyst. **A** is oxidized by molecular oxygen and generates V(V) species **B**, and **C** is formed through intramolecular hydrogen abstraction. To corroborate this reaction pathway, we examined the catalyst complex via ⁵¹V NMR spectroscopy. A weak and broad peak was detected at ca. δ -510 ppm in the ⁵¹V NMR spectrum (CDCl₃) of the mixture after reaction (See supporting

Figure 1. A plausible catalytic cycle

information).¹⁴ From this, we assume the formation of active catalytic V(V) species in this reaction. Elimination of H₂O₂ (**D**) and ligand exchange of product by alcohol (**E**) completes the catalytic cycle. We suppose that benzhydrols may generate H₂O₂, as a more active oxidant than molecular O₂, act as a ligand for the vanadium catalyst, or eliminate some active species to improve catalytic activity (See supporting information).¹⁵

Conclusion

In conclusion, we have developed a novel vanadium-catalyzed system for the oxidation of benzyl alcohol derivatives, using water as the sole solvent under atmospheric pressure of O₂. Furthermore, oxidation proceeds under open-air atmosphere, and the corresponding carbonyl compounds are obtained in good yields. The advantages of our oxidation method are three-fold: (1) special devices such as autoclaves are unnecessary; (2) there is no cost for the oxidant, as air functions as the terminal oxidant; (3) the gram-scale oxidation of several alcohols proceeds efficiently using water as a benign reaction medium. Finally, because our oxidation method is safe, operationally simple, and amenable to gram-scale synthesis under an air atmosphere, we expect this novel vanadium–bipyridyl ligand complex to be useful for green oxidation in organic synthesis and low-costly industrial chemical applications.

Experimental Section

General Information

¹H NMR spectra were recorded on a JEOL JNM-ECX400 (400 MHz) FT NMR system using CDCl₃ as the solvent with tetramethylsilane (TMS) as the internal standard. ¹³C NMR spectra were recorded on a JEOL JNM-ECX400 (100 MHz) FT NMR system using CDCl₃ as the solvent. Alcohols were prepared by reduction of the corresponding ketones with NaBH₄ (except **1a**, **1f**, **1g**, **1h**, **1i**, **3j**, and **3n**). Unless otherwise noted, other reactants and reagents were purchased from commercial source and used without further purification.

General procedure of Synthesis of substrates¹⁶

To a solution of ketone or aldehyde (20.0 mmol) in MeOH (50 mL) (or a mixture of MeOH and MeCN), NaBH₄ (40 mmol) was

added and stirred at room temperature. After confirming by TLC that the starting material was consumed entirely, the reaction mixture was poured into a separatory funnel, and organic layer was extracted with EtOAc. Extracted organic layers were washed with brine, and dried with anhydrous MgSO_4 , and concentrated to give the pure product.

Synthesis of $[\text{VO}(\text{t-Bubpy})_2]\text{SO}_4^{17}$

To a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridyl (930.4 mg, 3.5 mmol) in EtOH (40 mL) was added a solution of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (437.6 mg, 1.7 mmol) in EtOH (20 mL). After stirring for 2.5 h at room temperature, the solution was concentrated under reduced pressure, and the precipitate was filtered using diethyl ether and dried in vacuo to afford $[\text{VO}(\text{t-Bubpy})_2]\text{SO}_4$ as a green powder (700.6 mg). HR-ESI MS (MeOH) calcd for $\text{C}_{36}\text{H}_{49}\text{N}_4\text{O}_5\text{SV}[\text{M} + \text{H}] + 700.2863$, found 700.2881.

Oxidation of benzhydrols with molecular oxygen

Catalyst (0.005 mmol), ligand (0.01 mmol), and substrate (0.1 mmol) were placed in a 10 mL two necked flask, and then water (0.5 mL) was added. Next, the mixture was stirred at 90 °C for the appropriate time under O_2 (0.1 MPa, O_2 balloon). The yield of the product was confirmed by ^1H NMR spectroscopy using 1,2-diphenylethane as the internal standard, after extraction of the reaction mixture with diethyl ether. Purification of the products was carried out by a short pad of silica gel using ethyl acetate and hexane as eluent to afford the analytically pure ketones. The products were identified by comparison with the commercially available samples.

Oxidation of benzhyalcohols with molecular oxygen

$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (6.3 mg, 0.025 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (13.4 mg, 0.05 mmol), and *p*-nitrobenzhydrol (0.05 mmol) were placed in a 25 mL two necked round-bottomed flask, and then water (2.5 mL) was added. Next, the mixture was stirred, and then anhydrous MgSO_4 (902.8 mg, 7.5 mmol) was slowly added into the mixture (cooling by ice water). Then, substrate (0.5 mmol) was added into the mixture at room temperature, and the mixture was stirred at 90 °C for the appropriate time under O_2 (0.1 MPa, O_2 balloon). The yield of the product was confirmed by ^1H NMR spectroscopy using 1,2-diphenylethane as the internal standard. ^1H NMR spectroscopy using 1,2-diphenylethane as the internal standard, after extraction of the reaction mixture with diethyl ether. The product was identified by comparison with the commercially available sample.

Oxidation of alcohols under open-air atmosphere

$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (126.5 mg, 0.5 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (268.4 mg, 1 mmol), and *p*-nitrobenzhydrol (229.3 mg, 0.05 mmol) were placed in a 100 mL round-bottomed flask, and then water (50 mL) was added. Next, the mixture was stirred, and then anhydrous MgSO_4 (18.06 g, 150 mmol) was slowly added into the mixture (cooling by ice water). After that, substrate (10 mmol) was added into the mixture at room temperature, and the mixture was stirred at 90 °C for the appropriate time under open air atmosphere. After the reaction, the mixture was extracted with ethyl acetate and dried over anhydrous MgSO_4 . The extracts were concentrated in vacuo. Purification of the products was carried out by silica gel column chromatography using hexane and diethyl ether as eluent to afford the analytically pure ketones. In Table 7 (entries 3, 7 and 8), crude products were purified by recrystallization with ethyl acetate in refrigerator, afforded analytically pure ketones. The

product was identified by comparison with the commercially available sample using ^1H NMR spectroscopy.

Analytical Data.

Benzophenone^{18(a), 18(b), 18(c)} (**2a**, Scheme 5). White solid; Mp 47–48 °C; yield 1.7149 g (94%); ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.80 (m, 4H), 7.62–7.58 (m, 2H), 7.51–7.47 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 137.6, 132.4, 130.0, 128.2

4-Methoxyphenyl(phenyl)methanone^{18(b), 18(c), 18(j)} (**2b**, Table 7). White solid; Mp 56–57 °C; yield 1.9185 g (90%); ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 7.3 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.54–7.43 (m, 3H), 6.95 (d, J = 7.3 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.4, 163.1, 138.2, 132.4, 131.8, 129.6, 129.3, 128.1, 113.5, 55.4

4-Bromophenyl(phenyl)methanone^{18(a), 18(b), 18(j)} (**2c**, Table 7). White solid; Mp 74–75 °C; yield 2.2998 g (88%); ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.74 (m, 2H), 7.67–7.56 (m, 5H), 7.49–7.45 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.4, 137.0, 136.2, 132.6, 131.5, 131.4, 129.8, 128.3, 127.4

4-Nitrophenyl(phenyl)methanone^{18(b), 18(j)} (**2d**, Table 7). Yellow solid; Mp 136–137 °C; yield 1.1009 g (48%); ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 7.3 Hz, 2H), 7.66 (t, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.8, 149.8, 142.9, 136.3, 133.5, 130.7, 130.1, 128.7, 123.5

Bis(4-methylphenyl)methanone^{18(d), 18(k)} (**2e**, Table 7). White solid; Mp 87–88 °C; yield 1.3044 g (61%); ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.2 Hz, 4H), 7.27 (d, J = 8.2 Hz, 4H), 2.44 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 142.9, 135.2, 130.2, 128.9, 21.6

Phenyl(*p*-tolyl)methanone^{18(a), 18(b), 18(k)} (**2f**, Table 7). Yellow solid; Mp 52–53 °C; yield 1.7642 g (90%); ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.76 (m, 2H), 7.73–7.71 (d, J = 8.2 Hz, 2H), 7.58–7.54 (tt, J = 7.3 Hz, 1.37 Hz, 1H), 7.48–7.44 (m, 2H), 7.27 (d, J = 7.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 143.2, 137.9, 134.8, 132.1, 130.2, 129.9, 128.9, 128.1, 21.6

4-Chlorophenyl(phenyl)methanone^{18(b), 18(c), 18(k)} (**2g**, Table 7). White solid; Mp 70–71 °C; yield 1.9627 g (90%); ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.74 (m, 4H), 7.62–7.57 (m, 1H), 7.51–7.44 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.4, 138.8, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.3

Bis(4-methoxyphenyl)methanone^{18(c), 18(l)} (**2h**, Table 7). White solid; Mp 143–144 °C; yield 1.6673 g (69%); ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 7.3 Hz, 4H), 6.95 (d, J = 7.3 Hz, 4H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.3, 162.7, 132.1, 130.6, 113.3, 55.3

Bis(4-chlorophenyl)methanone^{18(c), 18(k)} (**2i**, Table 7). White solid; Mp 142–143 °C; yield 1.4536 g (57%); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 8.7 Hz, 4H), 7.47 (d, J = 8.2 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.2, 139.1, 135.5, 131.3, 128.8

1-Phenylpentan-1-one^{18(g)} (**4g**, Table 8). Colorless oil; yield 1.3454 g (83%); ^1H NMR (400 MHz, CDCl_3) δ 7.94–7.92 (m, 2H), 7.51–7.47 (m, 1H), 7.42–7.38 (m, 2H), 2.91 (t, J = 7.3 Hz, 2H), 1.69 (quint, J = 7.3 Hz, 2H), 1.38 (sextet, J = 7.3 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.8, 136.7, 132.4, 128.1, 127.6, 37.8, 26.0, 22.1, 13.6

Cyclohexyl(phenyl)methanone^{18(a), 18(m)} (**4i**, Table 8). White solid; Mp 54–55 °C; yield 1.519 g (81%); ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.78 (m, 2H), 7.38–7.25 (m, 3H), 3.15–3.08 (m,

1H), 1.75–1.06 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 203.2, 135.9, 132.3, 128.2, 127.9, 45.1, 29.0, 25.6, 25.5

1-Phenylbutan-1-one^{18(e), 18(f)} (**4j**, Table 8). Colorless oil; yield 1.2568 g (85%); ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.95 (m, 2H), 7.58–7.53 (m, 1H), 7.48–7.44 (m, 2H), 2.95 (t, *J* = 7.3, 2H), 1.78 (sextet, *J* = 7.3, 2H), 1.01 (t, *J* = 7.3, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 136.8, 132.5, 128.2, 127.7, 40.1, 17.4, 13.5

1-(4-Methoxyphenyl)butan-1-one^{18(e)} (**4k**, Table 8). Yellow oil; yield 1.630 g (92%); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.75 (sextet, *J* = 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.7, 163.1, 130.0, 130.0, 113.4, 55.2, 39.9, 17.8, 13.7

1-(4-Chlorophenyl)butan-1-one^{18(f), 18(n)} (**4l**, Table 8). White solid; Mp 36–37 °C; yield 1.9185 g (90%); ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 2.91 (t, *J* = 6.9 Hz, 2H), 1.76 (sextet, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 139.2, 135.3, 129.4, 128.8, 40.4, 17.6, 13.7

2-methy-1-Phenylpropan-1-one^{18(g), 18(h)} (**4m**, Table 8). Colorless oil; yield 1.3454 g (70%); ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.94 (m, 2H), 7.54–7.49 (m, 1H), 7.46–7.41 (m, 2H), 3.54 (sept, *J* = 6.9 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 204.1, 136.0, 132.6, 128.4, 128.1, 35.1, 18.9

1-Phenylheptan-1-one¹⁸⁽ⁱ⁾ (**4o**, Table 8). Colorless oil; yield 1.069 g (83%); ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.95 (m, 2H), 7.57–7.53 (m, 1H), 7.47–7.44 (m, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.74 (quint, *J* = 7.3 Hz, 2H), 1.40–1.30 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.6, 137.1, 132.8, 128.5, 128.0, 38.6, 31.7, 29.0, 24.3, 22.5, 14.0

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Graphical Abstract

Vanadium-Catalyzed Green Oxidation of Benzylic Alcohols in Water under Air Atmosphere

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