



# Cerium-photocatalyzed aerobic oxidation of benzylic alcohols to aldehydes and ketones

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## Letter

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## Abstract

We have developed a cerium-photocatalyzed aerobic oxidation of primary and secondary benzylic alcohols to aldehydes and ketones using inexpensive  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  as photocatalyst and air oxygen as the terminal oxidant.

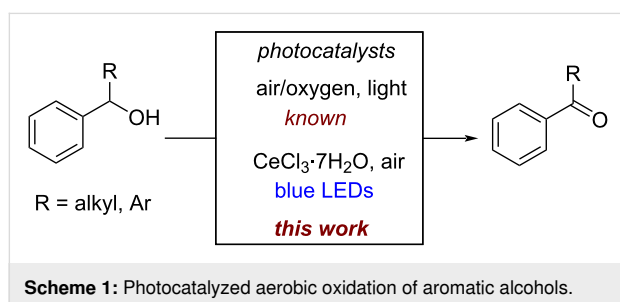
## Introduction

The selective oxidation of alcohols to carbonyl compounds [1,2] is an important process for producing a wide range of value-added fine chemicals [3-6]. In the traditional oxidation process stoichiometric amounts of oxidants such as  $\text{Br}_2$ ,  $\text{MnO}_2$ , hypervalent iodine reagents, chromium-based reagents, activated dimethyl sulfoxide,  $\text{KMnO}_4$ ,  $\text{OsO}_4$ , or metal-based catalysts and peroxide were used [7-17]. Most of these protocols produce harmful waste and some of the oxidizing reagents are considered toxic [7-17]. In order to overcome the limitations, various homogeneous and heterogeneous catalytic oxidation systems have been reported. Aerobic oxidation is particularly attractive as it allows the transformations under mild reaction conditions with molecular oxygen acting as the terminal oxidant

[13-33]. Most aerobic oxidation reactions utilize either metal complexes and nanoparticles or persistent radical reagents as catalysts [21].

In the past ten years, visible light-induced photocatalysis has emerged as an alternative to the classical conventional synthetic methods to construct carbon-carbon and carbon-heteroatom bonds [34-37]. As a mild, efficient, and environmentally friendly approach it has the potential to unlock unique reactions that are previously inaccessible under thermal conditions. Significant advances were made for the oxidation of benzylic alcohols by using metal-based photocatalysts [38-46] and metal-free photocatalysis [47-53] in combination with various oxidants,

such as TBHP and DDQ [54,55]. However, the reported methods require either specific nanoparticle catalysts [39–42] or the catalytic method is limited to electron-rich or electron-neutral benzylic alcohols [56]. An operationally simple method avoiding waste and potentially toxic transition-metal catalysts that is able to convert any benzylic alcohol selectively to the aldehyde or ketone is still desirable. Recently, cerium photocatalysis was introduced as a robust alternative to generate oxygen or carbon-centered radicals under mild reaction conditions [57–64]. CeCl<sub>3</sub> reacts via ligand-to-metal charge transfer generating oxygen-centered radicals, that lead to carbon-centered radicals through intra/intermolecular hydrogen atom transfer (HAT) processes, radical decarboxylative or radical deformylation [57–59]. In continuation of our research interest on visible-light-driven cerium photocatalysis [59,65], we herein report a mild aerobic photocatalytic oxidation of benzylic alcohols to aldehydes and ketones using 10 mol % CeCl<sub>3</sub>·7H<sub>2</sub>O (Scheme 1).



## Results and Discussion

A variety of reaction parameters was tested during the optimization of the reaction with 4-iodobenzyl alcohol (**1a**) as the model substrate and air as the oxidant (Table 1). The best results were found using 10 mol % CeCl<sub>3</sub>·7H<sub>2</sub>O as a photocatalyst and 10 mol % of NaHCO<sub>3</sub> as a base in CH<sub>3</sub>CN under blue LED irradiation at 50 °C for 35 h giving compound **2a** in 65% isolated yield (Table 1, entry 1). The product formation was reduced upon employing other cerium salts (Table 1, entries 2 and 3). Also, replacing NaHCO<sub>3</sub> by other bases such as K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> resulted in lower yields (30–40%) of product **2a** (Table 1, entries 4 and 5). In the absence of a base the reaction afforded product **2a** in 40% yield (Table 1, entry 6). The reaction worked with similar efficiency in CHCl<sub>3</sub> and DMF (Table 1, entries 7 and 8), while other solvents such as toluene and EtOAc gave **2a** in moderate yields (Table 1, entries 9 and 10). THF was found to be less effective in this oxidation reaction (Table 1, entry 11). Performing the reaction at 35 °C gave **2a** in a moderate yield of 35% (Table 1, entry 12). Employing an external oxidant such as (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> instead of air diminished the yield (Table 1, entry 13). The substitution of air with a balloon of oxygen afforded **2a** in 25% yield (Table 1, entry 14), while employing an argon atmosphere led to only trace amounts

of the product (Table 1, entry 15). Additionally, control experiments indicated that catalytic amounts of the cerium salt, air atmosphere and light irradiation were necessary for the reaction to occur (Table 1, entries 16 and 17).

**Table 1:** Optimization of the reaction conditions.<sup>a</sup>

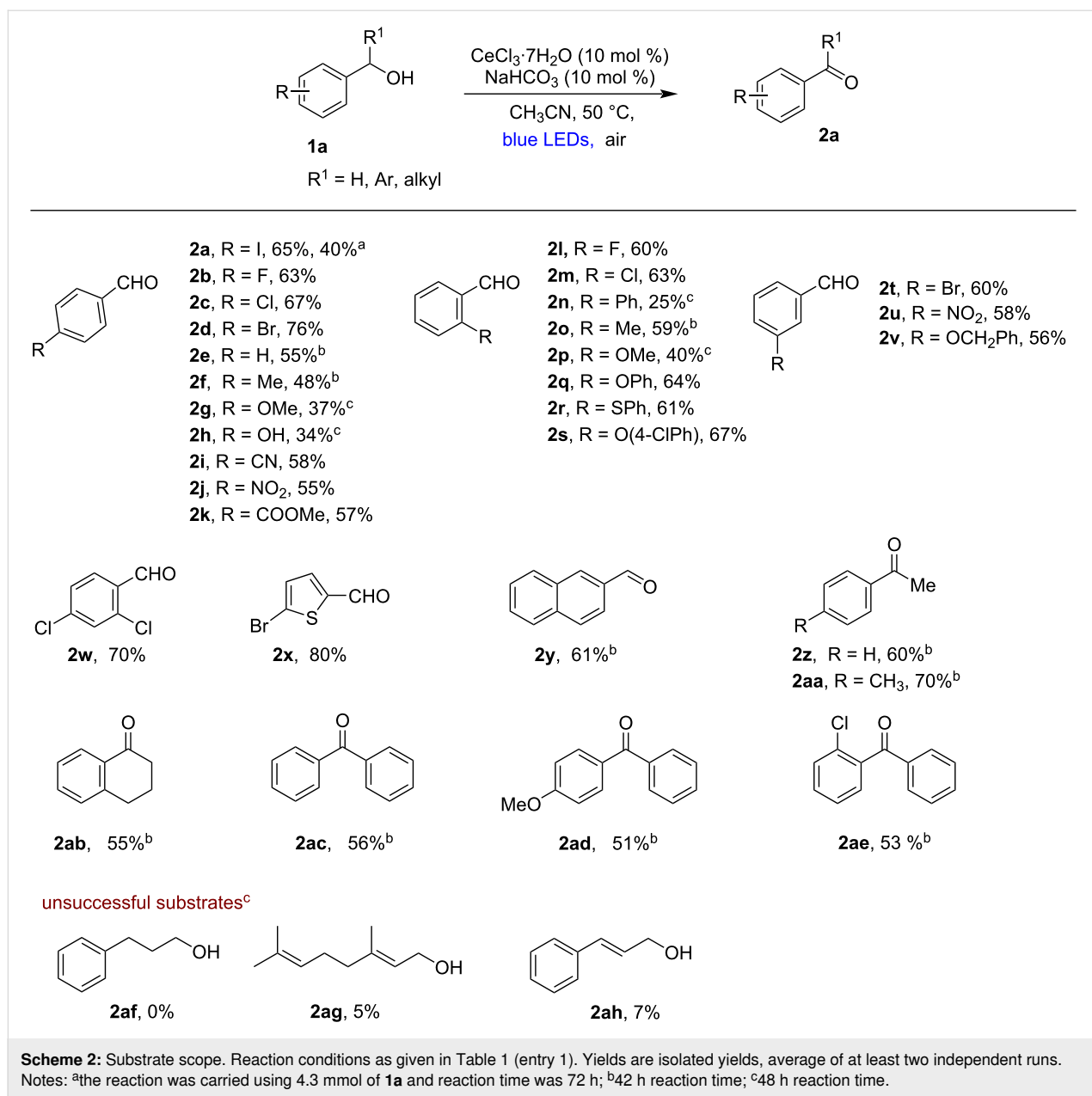


entry	deviation from standard conditions	<b>2a</b> (%) <sup>b</sup>
1	none	70 (65) <sup>c</sup>
2	CeCl <sub>3</sub> instead of CeCl <sub>3</sub> ·7H <sub>2</sub> O	60
3	( <i>n</i> -Bu <sub>4</sub> N) <sub>2</sub> Ce <sup>IV</sup> Cl <sub>6</sub> instead of CeCl <sub>3</sub> ·7H <sub>2</sub> O	42
4	K <sub>2</sub> CO <sub>3</sub> instead of NaHCO <sub>3</sub>	40
5	Na <sub>2</sub> CO <sub>3</sub> instead of NaHCO <sub>3</sub>	30
6	without base	40
7	CHCl <sub>3</sub> instead of CH <sub>3</sub> CN	56
8	DMF instead of CH <sub>3</sub> CN	60
9	toluene instead of CH <sub>3</sub> CN	30
10	EtOAc instead of CH <sub>3</sub> CN	21
11	THF instead of CH <sub>3</sub> CN	5
12	at 35 °C instead of 50 °C	35
13	with 2.0 equiv of (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> instead of air	28
14	with O <sub>2</sub> balloon instead of air	25
15	under argon instead of air	trace
16	without CeCl <sub>3</sub> ·7H <sub>2</sub> O	0
17	without light	trace

<sup>a</sup>Standard conditions: **1a** (0.2 mmol), CeCl<sub>3</sub>·7H<sub>2</sub>O (10 mol %), NaHCO<sub>3</sub> (10 mol %), CH<sub>3</sub>CN (0.1 M) at 50 °C, 455 nm blue LED for 35 h. <sup>b</sup>NMR yields using trimethoxybenzene as internal standard.

<sup>c</sup>Isolated yield.

With the optimized reaction parameters in our hands, we next explored the substrate scope of the reaction. As shown in Scheme 2, a broad range of primary and secondary benzylic alcohols was converted into the corresponding aldehydes and ketones. Various electron-withdrawing *para*-halo-substituted benzylic alcohols **1a–d** were tested under the optimized reaction conditions and gave the corresponding halo-substituted benzaldehydes **2a–d** in good yields. The oxidation of simple benzyl alcohol (**1e**) under our reaction conditions gave benzaldehyde (**2e**) in 55% yield. A variety of electron-donating *para*-substituted benzyl alcohols (**1f–h**) gave lower isolated yields of the corresponding benzaldehydes **2f–h**. Our methodology tolerates a variety of functional groups containing benzylic alcohols such as -OH (**1h**), -CN (**1i**), -NO<sub>2</sub> (**1j**), methyl ester (**1k**), and benzyloxy (**1v**) to produce the corresponding alde-



hydres (**2h–k** and **2v**) in moderate yields. Next, electronically different *ortho*-substituted benzylic alcohols were tested and 2-fluoro (**1l**) and 2-chloro (**1m**) benzyl alcohols gave the aldehydes **2l** and **2m** in good yields. The *o*-phenyl-substituted benzylic alcohol (**1n**) afforded biphenyl-2-carbaldehyde (**2n**) in only low yield (25%) probably due to steric reasons. The *o*-methyl (**1o**) and *o*-methoxy (**1p**) benzylic alcohols yielded the corresponding benzaldehydes **2o** and **2p** in moderate yields and to our surprise we did not observe any oxidation of the methyl or methoxy groups via hydrogen atom transfer processes [57]. Interestingly, we found that a variety of *ortho*-phenoxy-substituted benzylic alcohols (**1q**, **1s**) were oxidized under our reaction conditions giving the corresponding aldehydes (**2q**, **2s**) in

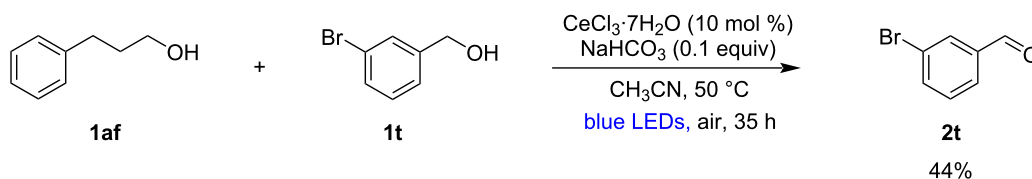
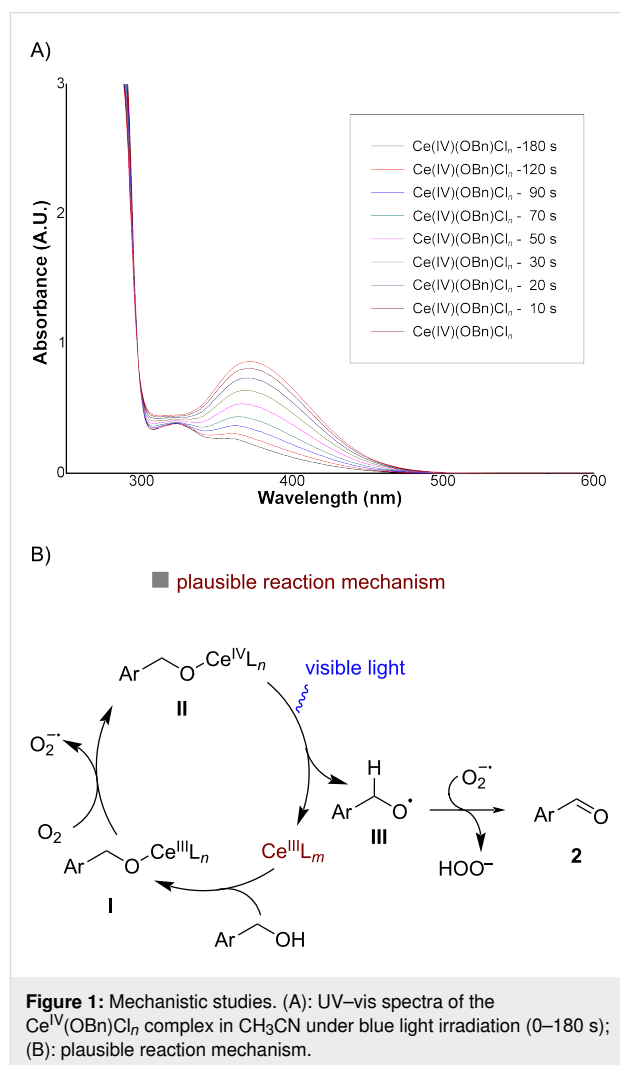
good yields. Also, the *meta*-substituted benzylic alcohols **1t–v** reacted to the corresponding benzaldehydes in good yields in our reaction conditions. *Ortho/para*-disubstituted benzylic alcohol **1w** gave 2,4-dichlorobenzaldehyde (**2w**) in 70% yield. The sulfur-containing compounds 4-(phenylthio)benzyl alcohol (**1r**) and the heterocyclic compound thiophene-2-ylmethanol (**1x**) gave the corresponding aldehydes **2r** and **2x** in 61 and 80% yield, respectively. Finally, 2-naphthylmethanol (**1y**) was subjected to the reaction conditions and gave 2-naphthaldehyde (**2y**) in good yield (61%).

Next, the scope of secondary benzylic alcohols was tested in our reaction conditions. Substituted 1-phenylethanols such as

**1z**, **1aa**, tetralol (**1ab**), diphenyl methanol (**1ac**) and derivatives thereof with substituents of different electronic nature such as **1ad** and **1ae** gave the ketones **2z**, **2aa**, **2ab**, **2ac**, **2ad**, and **2ae** in good yields. However, the primary aliphatic alcohol 3-phenylpropanol (**1af**) did not provide the desired aldehyde at all, and allylic alcohols such as geraniol (**1ag**) and cinnamyl alcohol (**1ah**) afforded the aldehydes **2ag** and **2ah** in very low yields (5 and 7%, respectively). In addition, when the mixture of 3-phenylpropanol (**1ah**) and 3-bromobenzyl alcohol (**1t**) was subjected to the standard reaction conditions, we observed the selective oxidation of the benzylic alcohol giving the expected product in 44% yield (Scheme 3).

The efficiency of this cerium-photocatalyzed aerobic oxidation of alcohols prompted us to conduct some preliminary mechanistic studies (Figure 1). As anticipated, the ON/OFF irradiation experiments confirmed that our reaction required a continuous blue light irradiation (see Supporting Information File 1). The inhibition of the catalytic cycle upon the addition of TEMPO revealed that the reaction proceeds through radical intermediates. Next, we carried out UV–vis monitoring experiments in order to verify whether the interaction with the substituted benzyl alcohols and  $\text{Ce}^{\text{IV}}$  could lead to a ligand-to-metal charge transfer (LMCT) process, which reduces the  $\text{Ce}^{\text{IV}}$  species to  $\text{Ce}^{\text{III}}$ , similarly as reported by Zuo and co-workers [57]. We chose  $(n\text{-Bu}_4\text{N})_2\text{Ce}^{\text{IV}}\text{Cl}_6$  as the  $\text{Ce}^{\text{IV}}$  source to ensure a sufficient solubility in organic solvents and to facilitate the detection of the species. The  $\text{Ce}^{\text{IV}}(\text{OBn})\text{Cl}_n$  complex was prepared by mixing the  $(n\text{-Bu}_4\text{N})_2\text{Ce}^{\text{IV}}\text{Cl}_6$  complex with BnOH under basic conditions. The UV–vis spectra of the  $\text{Ce}^{\text{IV}}(\text{OBn})\text{Cl}_n$  complex displayed a band resembling the LMCT band of known cerium–alkoxide complexes, showing considerable overlap with the blue LED region, thus suggesting that the  $\text{Ce}^{\text{IV}}(\text{OBn})\text{Cl}_n$  species could be photoexcited (Figure 1A). We then analyzed UV–vis spectra of the  $\text{Ce}^{\text{IV}}(\text{OBn})\text{Cl}_n$  complex recorded after irradiation with blue light at different time intervals. As shown in Figure 1A, the absorption spectrum of the  $\text{Ce}^{\text{IV}}(\text{OBn})\text{Cl}_n$  complex gradually shifted from  $\lambda_{\text{max}} = 375$  nm to  $\lambda_{\text{max}} = 325$  nm upon irradiation, which indicates a photoinduced  $\text{Ce}^{\text{IV}}\text{-OBn}$  homolytic cleavage to generate a  $\text{Ce}^{\text{III}}$  complex and a benzyloxy radical. Although the exact catalytic cycle

of our reaction remains to be elucidated, we propose a plausible reaction mechanism based on our observations and known literature precedents (Figure 1B) [57,59,66–69]. Under aerobic conditions the catalytic  $\text{Ce}^{\text{III}}(\text{OBn})\text{L}_n$  species **I** (in situ derived by the reaction of  $\text{CeCl}_3$  ( $\text{Ce}^{\text{III}}\text{L}_n$ ) with the substrate benzyl alcohol, BnOH) could be oxidized to  $\text{L}_n\text{Ce}^{\text{IV}}\text{-OBn}$  complex **II** [67–69]. During this process  $\text{O}_2$  is converted into a superoxide radical anion  $\text{O}_2^{\bullet-}$ . Photolysis of the  $\text{Ce}^{\text{IV}}\text{-OBn}$  complex (**II**), leads to the formation of the corresponding benzyloxy radical



**Scheme 3:** Selective oxidation of 3-bromobenzyl alcohol in the presence of 3-phenylpropanol. Compound **1af** was recovered unchanged from the reaction mixture.

(III) and regenerates the Ce<sup>III</sup> species. A further abstraction of a benzylic hydrogen atom by the peroxide radical then generates the final product **2** [48]. However, at this moment we cannot exclude the involvement of possible intermolecular HAT or 1,2-HAT from the intermediate III to generate the product **2**.

## Conclusion

In summary, we have developed a catalytic aerobic oxidation of benzylic alcohols to the corresponding aldehydes without further oxidation and formation of benzoic acids. A variety of primary and secondary benzylic alcohols were converted into the corresponding aldehydes and ketones in good to moderate yields using commercially available and inexpensive CeCl<sub>3</sub>·7H<sub>2</sub>O as a photocatalyst and air as an oxidant.

## Supporting Information

### Supporting Information File 1

Full experimental details, compound characterization, and copies of NMR spectra.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-17-121-S1.pdf>]

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