# Light-Mediated Aerobic Oxidation of C(sp3)−H Bonds by a Ce(IV) Hexachloride Complex

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ARTICLE

# Light-Mediated Aerobic Oxidation of C($sp^3$)–H Bonds by a Ce(IV) Hexachloride Complex

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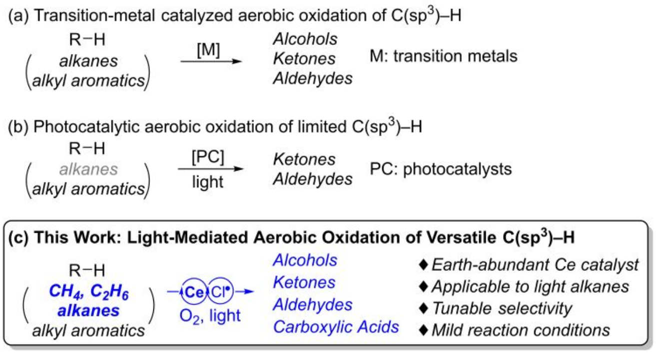
A photochemical C($sp^3$)–H oxygenation of alkane and arene substrates catalyzed by $[NEt_4]_2[Ce^{IV}Cl_6]$ under mild conditions (1 atm, 25°C) is described. Time-course studies reveal that the hydrocarbons are oxidized in a stepwise fashion to afford alcohols, aldehydes, ketones, and carboxylic acids. The catalyst resting state, $[Ce^{IV}Cl_6]^{2-}$, is observed by UV-visible spectroscopy. On/off light-switching experiments, quantum yield measurements, and the absence of a kinetic isotope effect on parallel C−H/C−D functionalization suggest that ligand-to-metal charge transfer of $[NEt_4]_2[Ce^{IV}Cl_6]$ to generate Cl• is the turnover-limiting step. The involvement of a highly reducing excited-state $[NEt_4]_3[Ce^{III}Cl_6]^*$ species as well as photo-excited aldehyde, under black light irradiation appears to facilitate the conversion of primary alcohols and aldehydes to carboxylic acids. Remarkably, this approach is found to be capable of direct activation of light alkanes, including methane and ethane.

## Introduction

The oxygenation of organic compounds is a fundamental reaction in biology and chemistry.[1-3] In biology, cells use oxygen to convert glucose into energy in cellular respiration.[4] Oxidative reactions, including C−H oxygenations, play a significant role in organic transformations and chemical synthesis.[5-8] The C−H oxygenation of hydrocarbons has been extensively applied to afford valuable products such as fine chemicals, feedstocks, and pharmaceuticals.[9-16] Previous approaches to C−H oxygenation, however, typically require excess terminal oxidants (e.g., iodosobenzene, $^t$butyl hydroperoxide),[15, 16] harsh reaction conditions (e.g., elevated temperature and pressure), and noble-metal catalysts (e.g., Pd, Ir, and Pt) and, therefore, are not environmentally benign (Scheme 1a).[9-16] The abundance of molecular oxygen in the Earth's atmosphere renders catalytic C−H oxygenation using $O_2$ as the terminal oxidant particularly attractive.[11-13, 15-20] Additionally, low-cost metal catalysts are needed for practical applications. The development of new methods utilizing molecular oxygen and earth-abundant catalysts to achieve the C−H oxygenation of hydrocarbons, including light alkanes, is, therefore, a high priority.

Photoredox catalysis provides an opportunity to achieve C($sp^3$)−H oxygenations under mild and environmentally friendly conditions. Molecular catalyst systems that are low-cost, benign, and use molecular oxygen, have been achieved for light-mediated C($sp^3$)−H oxygenations, such as decatungstate (under UVA light), uranyl, acridinium and flavin-based photocatalysts (under blue or purple light), and others (Scheme 1b).[21-26] Recently, Cl• has been studied extensively and employed in alkylarene oxygenation reactions. Recently, Hu, Jiang and Zeng employed iron catalysts[27-29]; Wang's group used HCl as a catalyst and Shi and co-workers disclosed cerium photoredox catalysis[30] during the final stages of the investigations presented herein. However, the substrate scope of these systems was rather restricted and was generally limited to alkyl aromatics.[31-38] Notably, Fukuzumi and others reported that stronger alkyl C−H bonds, such as those in cyclohexane, could be photochemically activated by chlorine radical (Cl•) under aerobic conditions. However, the generation of the oxidation products in those studies was not particularly selective.[39, 40] These constraints inspired us to develop an alternative strategy for light-mediated catalytic C($sp^3$)−H oxygenations with broader substrate scope and controllable selectivity.



**Scheme 1** Overview of the established strategies (**a** and **b**) and our strategy **c** for light-mediated oxygenation of C($sp^3$)–H bonds.

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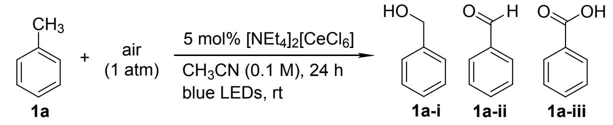
**Table 1** Optimization of the reaction conditions using blue LEDs.



| Entry | Variations from standard conditions[a] | $^1H$ NMR AY (%)[b] | | | |
|---|---|---|---|---|---|
| | | 1a-i | 1a-ii | 1a-iii | total |
| 1 | 18 h, 1 atm air | ≈ 5 | 21 | 26 | 52 |
| 2 | 18 h, 1 atm $O_2$ | ≈ 5 | 25 | 28 | 58 |
| 3 | none | ≈ 5 | 24 | 29 | 58 |
| 4 | in the dark | – | – | – | – |
| 5 | in the dark, 80°C | – | – | – | – |
| 6 | black light[c] | – | – | ≈ 5 | ≈ 5 |
| 7 | no $[NEt_4]_2[Ce^{IV}Cl_6]$ | – | – | – | – |
| 8 | 1 atm $N_2$ | – | – | – | – |
| 9 | DMF instead of $CH_3CN$[d] | – | – | – | – |
| 10 | DME instead of $CH_3CN$[e] | – | – | – | – |
| 11 | 10 mol% $[NEt_4]_2[Ce^{IV}Cl_6]$ | – | 34 | 40 | 74 |
| 12 | 48 h, 1 atm air | – | 36 | 47 | 83 |

[a] Initial conditions: 0.4 mmol toluene, 0.02 mmol **I**, 4 mL $CH_3CN$ in a 8 mL sample vial, irradiated with a Kessil A160WE blue LED lamp with fan cooling at room temperature (rt, 298 K) under aerobic conditions for 24 h. [b] Yield determined by $^1H$ NMR spectroscopy with 1,4-dioxane as an internal standard. [c] The reaction was irradiated with four 24 W (100 W equivalent) CFL black light bulbs. [d] DMF = dimethylformamide. [e] DME = dimethoxyethane.

Herein, we report the light-mediated oxygenation of various C(sp$^3$)–H bonds in hydrocarbons catalyzed by $[NEt_4]_2[Ce^{IV}Cl_6]$ (**I**) with $O_2$ as the terminal oxidant (Scheme 1c). The influence of radiation wavelengths on product selectivities and yields was investigated, and the crucial role of light frequency on the catalytic cycle has been revealed.

It was proposed that chlorine radical (Cl•) was responsible for the C(sp$^3$)–H bond cleavage,[41-49] consistent with recent work from our group, where the generation of Cl• radicals was demonstrated as the rate-limiting step, and the Cl• reactivity could be altered by the addition of suitable additives (alcohols and arenes).[50] The oxygenation of gaseous alkanes (i.e., $CH_4$ and $C_2H_6$) mediated by $[NEt_4]_2[Ce^{IV}Cl_6]$ was studied with the goal of transformation of light alkanes into liquid fuels under mild conditions, in contrast with ceria based catalysts that employ harsh conditions.[51, 52]

## Results and discussion

Our previous studies indicated that the C(sp$^3$)−H bond of toluene was activated by catalytic $[NEt_4]_2[Ce^{IV}Cl_6]$ using visible light irradiation under anaerobic conditions.[53] This finding led us to question whether photoredox catalyzed oxygenation of C(sp$^3$)−H bonds of hydrocarbons could be achieved by $[NEt_4]_2[Ce^{IV}Cl_6]$ under aerobic conditions. Toluene (**1a**) was selected as the model substrate for studying oxygenation in the presence of dioxygen due to its moderate C−H bond strength (bond dissociation energy [BDE] = 88.5 kcal/mol).[54] The study was initiated with blue light irradiation of a 0.1 M solution of toluene with 5 mol% $[NEt_4]_2[Ce^{IV}Cl_6]$ in acetonitrile ($CH_3CN$) at room temperature (298 K) for 18 h under 1 atm of air. The oxidation products PhCHO (**1a-ii**, BDE of the formyl C−H bond = 89 kcal/mol)[54] and $PhCO_2H$ (**1a-iii**) were observed in 21% and 26% assay yield, respectively (AY, determined by $^1H$ NMR integration against an internal standard) (Table 1, entry 1). Benzyl alcohol is presumably an intermediate in this process. However, the benzylic C–H bonds are notably weaker and more reactive in benzyl alcohol (BDE = 80 kcal/mol)[54] than in toluene, so it is not surprising that benzyl alcohol is only observed in the initial stage of the reaction. The AYs did not change significantly when the reaction was conducted under 1 atm of dioxygen under otherwise identical conditions (entry 2). Increasing the reaction time to 24 h increased the reaction AY to 58% (entry 3). Thus, 24 h was set as the standard reaction time. No reaction was observed in the dark either at room temperature (entry 4) or 80 °C (entry 5), suggesting that product formation is light-mediated.

We next conducted control experiments to verify the importance of the reaction components. The selection of light frequency is critical in light-mediated reactions. We were surprised to find that there was no conversion observed when the reaction was irradiated with black light ($\lambda_{max} = 330$ nm) instead of blue light ($\lambda_{max} = 467$ nm entry 6). No product was observed in the absence of the cerium catalyst **I** (entry 7) or molecular oxygen (entry 8). The oxidation reaction proved to be sensitive to the type of solvent: no oxidation of toluene was detected in dimethylformamide (DMF) or dimethoxyethane (DME), (entries 9 and 10).[55] The absence of products was presumably due to the limited solubility of **I** in DME and its relative instability in DMF during the reaction.

We next examined the evolution of toluene oxidation products through a time-course study using $^1H$-NMR spectroscopy (Figure 1 and Section II of the Supplemental Information). Over the 24 h course of the oxidation, a low concentration of $PhCH_2OH$ (**1a-i**) was observed in the initial stage of the reaction that was maintained as the reaction proceeded (Figure 1, green trace), indicating that the oxidation of $PhCH_2OH$ is kinetically facile relative to toluene. The production of benzaldehyde (Figure 1, blue trace) and benzoic acid (Figure 1, red trace) occurs through the oxidation of $PhCH_2OH$. The observation of $PhCH_2Cl$ is attributed to radical coupling of Cl• with the benzylic radical (Figure 1, yellow trace) and is consistent with the proposal that Cl• is the active oxidant. The steady-state concentration of $PhCH_2Cl$ ($\approx$ 10 %) suggests that it can be converted

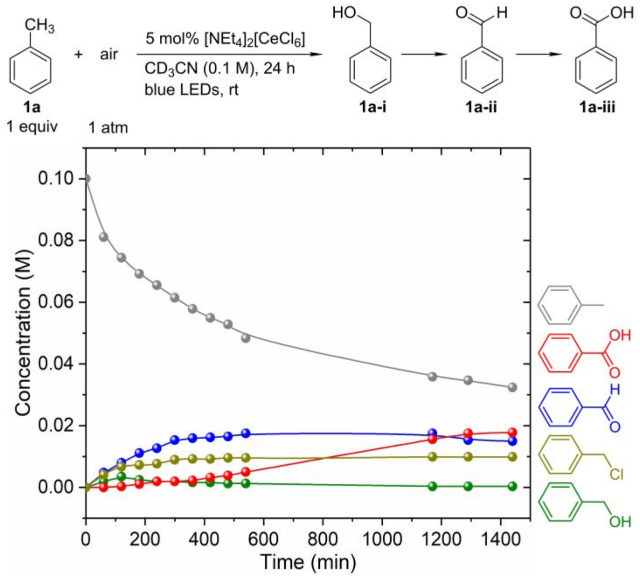
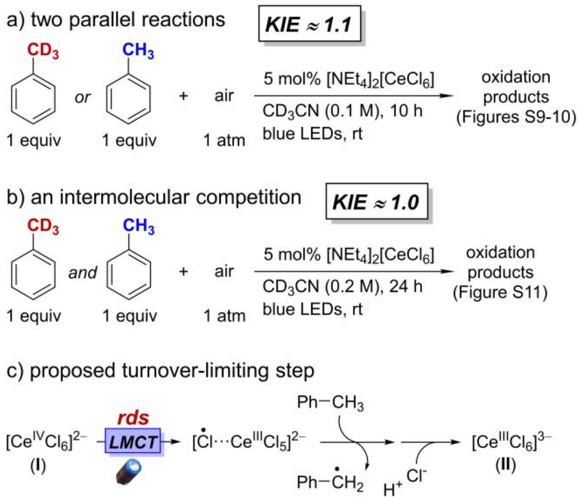


**Fig. 1** Time-course studies of C-H oxygenation of toluene by $^1H$ NMR spectroscopy: distribution of oxidation products. Reaction conditions: 0.1 M toluene, 0.005 M **I** (5 mol%), 0.5 mL $CD_3CN$ in an NMR tube (0.38 mm thickness), irradiated with a Kessil A160WE blue LED lamp with fan cooling at 298 K under aerobic conditions for 24 h.



**Scheme 2** Kinetic isotope effect experiments: a) two parallel reactions, b) an intermolecular competition, and c) the proposed turnover-limiting step (TLS). Reaction conditions: a) 0.05 mmol $PhCH_3$ or $PhCD_3$, 0.0025 mmol **I**, 0.5 mL $CD_3CN$ in an NMR tube (0.38 mm thickness); b) 0.2 mmol $PHCH_3$ and $PhCD_3$, 0.01 mmol **I**, 2 mL $CD_3CN$ in an 8 mL sample vial. Reactions were irradiated with a Kessil A160WE blue LED lamp with fan cooling at 298 K.

into oxidation products PhCHO or $PhCO_2H$ (Figure S17) and that catalyst degradation through chlorine sequestration with the formation of benzyl chloride is reversible. The addition of exogenous $[NEt_4][Cl]$ was envisioned to provide a chloride source, which is partially consumed in the formation of benzyl chloride.[53] Notably, the addition of $[NEt_4][Cl]$ led to a decrease in oxidation products and an increase in side products, such as benzyl chloride (Figure S5). The formation of benzyl hydroperoxide was negligible (< 5%) and only observed in the first hour over the time-course study (Figure S5). The detection of benzyl hydroperoxide indicated that the trapping of benzyl radical by dioxygen is involved in the reaction mechanism.

To probe the reaction mechanism, kinetic isotope effect (KIE) studies on the Ce-catalyzed C–H oxygenation of toluene were conducted (Section IV of the Supplemental Information). A parallel KIE study with $PhCH_3$ and $PhCD_3$ revealed a KIE of 1.1. This small KIE indicates that the C–H/C–D cleavage is not involved in the turnover-limiting step (Scheme 2a and Figures S9–10).[56, 57] A KIE value for an intermolecular competition experiment, in which the reaction was conducted with equimolar amounts of $PhCD_3$ and $PhCH_3$ in the same reaction vessel, was found to be 1.0 (Scheme 2b and Figure S11).

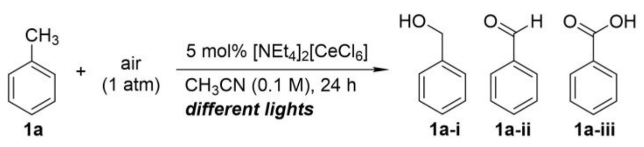
These results, together with the on-off experiments and quantum yield measurements (vide infra), support the hypothesis that the photo-induced generation of Cl• is likely the turnover-limiting step, which is followed by hydrogen atom transfer (HAT) from toluene (Scheme 2c).[58]

Having established the turnover-limiting step, we sought to determine if different light wavelengths would impact the distribution of the oxidation products (i.e., the ratio of $PhCO_2H$ to PhCHO).[59] The influence of irradiation wavelength on photocatalysis has been explored previously, although heterogeneous catalysts were used in most of these studies.[60-64] Here, under purple light ($\lambda_{max}$ = 390 nm) irradiation, the overall yield of toluene oxygenation products was found to be similar to that with blue light (Table 2, entries 1 vs. 2); however, the selectivity shifted to favor the formation of benzoic acid ($PhCO_2H$ : PhCHO ranged from 1.2 to 1.9 (Table 2, entries 1 vs. 2). This observation implies that the selectivity of C–H oxygenation is affected by the irradiation with different wavelengths ($\lambda_{max}$), which provides an opportunity to optimize the reaction using different light sources.[65] Based on previous studies, a critical step in the catalytic process is the oxidation of Ce(III) back to Ce(IV).[53, 55] $[NEt_4]_3[Ce^{III}Cl_6]$ (**II**) is a weak reductant (half-wave potential, $E_{1/2} \approx 0.03$ V vs. $Fc^+/Fc$), but the photoexcited state of $[Ce^{III}Cl_6]^{3-*}$ (**III**) is a strong reductant ($E_{1/2} \approx -3.45$ V vs. $Fc^+/Fc$).[53] We hypothesized that use of the black light in the catalyst reoxidation step might provide an opportunity to impact catalyst reactivity/selectivity by facilitating the reduction of oxidized intermediates (i.e., peroxides).

We, therefore, set out to examine the impact of a second light source on the oxygenation process.[66-68] We found that the overall yield of toluene oxygenation was not impacted when blue and black lights were used simultaneously (Table 2, entries 3 vs. 1). The selectivity of products, however, was impacted and favored $PhCO_2H$ ($PhCO_2H$ : PhCHO = 2.0). Employing a combination of purple/black lights resulted in an increase in yield (78%) and selectivity ($PhCO_2H$ : PhCHO = 2.9) (Table 2, entry 4), revealing that the influence of light source on catalytic oxygenation is considerable and merits further attention.

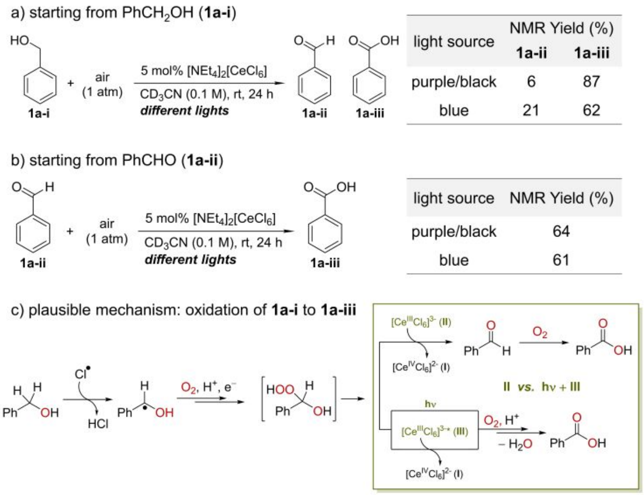
To further understand how the light source influences the reaction outcome, control experiments were performed on reaction substrates and intermediates using different light sources. Product distributions were analyzed after a 24-h reaction period (Section VIII-X of the Supplemental Information). Initially, *p*-tolunitrile was employed as substrate. Irradiation with a combination of purple and black lights resulted in more carboxylic acid generated (21%) than blue light (trace yield) (Figure S17). When benzyl chloride was use as substrate, it showed the same behaviour (Figure S18).

**Table 2** Influence of radiation wavelengths on C–H oxygenation of toluene.



| Entry | Light source[a] | NMR AY (%)[b] | | | | Selectivity (**1a-iii**/**1a-ii**) |
|---|---|---|---|---|---|---|
| | | 1a-i | 1a-ii | 1a-iii | total | |
| 1[c] | blue LED | ≈ 5 | 24 | 29 | 58 | 1.2 |
| 2 | purple LED[d] | ≈ 5 | 19 | 37 | 61 | 1.9 |
| 3[e] | blue LED & black light | ≈ 5 | 16 | 32 | 53 | 2.0 |
| **4[f]** | **purple LED & black light** | **≈ 5** | **19** | **54** | **78** | **2.9** |
| 5[g] | black light | – | – | 84[g] | – | – |

[a] General reaction conditions: 0.4 mmol toluene, 0.02 mmol **I**, 4 mL $CH_3CN$, irradiated with *different lights* at 298 K under aerobic conditions for 24 h. [b] Assay yield determined by $^1H$ NMR spectroscopy with 1,4-dioxane as an internal standard. [c] Entry 1 in Table 1. [d] A Kessil PR160-390 LED lamp ($\lambda_{max}$ = 390 nm). [e] A Kessil A160WE blue LED lamp ($\lambda_{max}$ = 467 nm) and four 24 W (100 W equivalent) CFL black light bulbs ($\lambda_{max}$ = 330 nm). [f] A Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL black light bulbs. [g] $[NEt_4]_2[Ce^{IV}Cl_6]$: 0.0 M; benzaldehyde (**1a-ii**): 0.04 M; toluene: 0.1 M; yield of **1a-iii** was based on 0.04 M benzaldehyde. Benzoic anhydride was included in the benzoic acid yield for convenience.



| light source | NMR Yield (%) 1a-ii | NMR Yield (%) 1a-iii |
|---|---|---|
| purple/black | 6 | 87 |
| blue | 21 | 62 |

| light source | NMR Yield (%) |
|---|---|
| purple/black | 64 |
| blue | 61 |

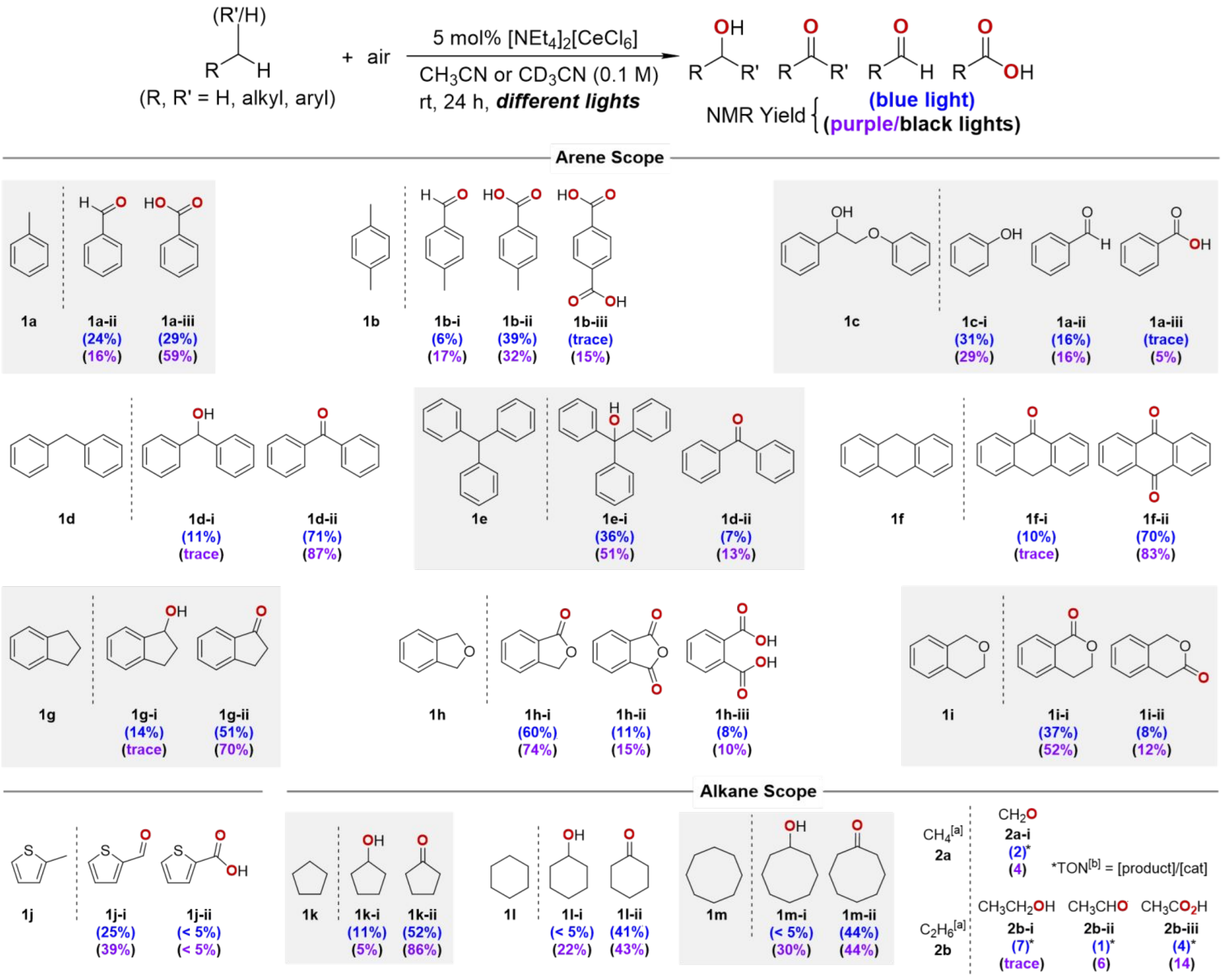
**Scheme 3** The influence of radiation wavelengths on difference steps in the C–H oxygenation of toluene: a) oxidation of $PhCH_2OH$ to PHCHO and $PhCO_2H$, b) oxidation of PHCHO to $PHCO_2H$, and c) a plausible reaction pathway for the oxidation of $PhCH_2OH$ to $PHCO_2H$ via HAT.

Control experiments were then performed on $PhCH_2OH$ (**1a-i**), PHCHO (**1a-ii**) and $PhC(CH_3)_2OOH$. Irradiation of $PhCH_2OH$ under catalytic conditions with purple/black light gave $PhCO_2H$ and PhCHO with a selectivity of 14.5 in a combined AY of 93% (Scheme 3a). Using only blue light led to 83% AY but with decreased selectivity of 3.0. We next examined the oxidation of PhCHO to $PhCO_2H$. With purple/black or blue light irradiation, both reactions proceeded with similar AY (61–64%, Scheme 3b). The difference in product distributions observed in Scheme 3a and the same AY in Scheme 3b, suggests that there is one reaction pathway producing $PhCO_2H$ (**1a-iii**) from $PhCH_2OH$ (**1a-i**) that bypasses the formation of PhCHO (**1a-ii**).

The light-mediated oxidation of **1a-i** to **1a-iii** has been proposed to proceed via a hydroperoxide intermediate, PhCH(OOH)OH.[69] As a model peroxide for this intermediate $PhC(CH_3)_2OOH$ was chosen (see Section X of the Supplemental Information). We found that $PhC(CH_3)_2OOH$ was reactive under light irradiation without the cerium catalyst, especially under the purple/black light combination (Figure S23–S25). This indicates that $PhC(CH_3)_2OOH$ can absorb light (hν), causing its decomposition by O–O bond cleavage.[70] In addition, under irradiation $PhC(CH_3)_2OOH$ is consumed faster in the presence of the cerium(III) catalyst. We hypothesize that the black light photoexcites $[NEt_4]_3[Ce^{III}Cl_6]$ species (**II**) to $[NEt_4]_3[Ce^{III}Cl_6]^*$, which reduces the peroxide. In the catalytic oxidation of benzyl alcohol, we propose that the acceleration of the reaction by the purple/black light combination is due to 1) the light absorption by the peroxide (see Supplemental Information, section X) and 2) the generation of the strong photoreductant $[NEt_4]_3[Ce^{III}Cl_6]^*$ (**III**),[53] ultimately generating benzoic acid. At this point, the origin of the different products with purple/black light irradiation is speculated to arise by two possible pathways. One involves reaction of excited state Ce(III) reduction of peroxy intermediates (Scheme 3c). The other involves direct photon absorption by benzylic peroxide intermediates and further reactions. The exact mechanism of the formation of benzoic acid, however, remains under investigation.[71]

A side reaction for benzaldehyde under black light irradiation was also considered (See Supplemental Information, Section IX). The triplet excited state of benzaldehyde (**1a-ii**) was reported to act as a triplet sensitizer capable of C–H activation.[72-75] A control experiment to probe toluene activation with benzaldehyde as catalyst under black light irradiation was carried out under air (Table 2, entry 5). This control experiment showed that the most significant reaction promoted by benzaldehyde was its oxidation to benzoic acid and benzoic anhydride (84% combined yield after 24 h). This outcome is likely due to either the excited triplet aldehyde reacting with triplet oxygen or singlet aldehyde with excited singlet oxygen via photosensitization.[76-78] Toluene activation, under these conditions, was not detected.

After investigating the influence of the light sources, we turned to examination of the substrate scope. A variety of hydrocarbons and heteroatom-containing compounds with diverse structures were tested (Scheme 4) under blue light or purple/black light irradiation. In general, better yields and higher selectivity was observed under the dual irradiation conditions. The reaction with para-xylene (**1b**) shows that oxygenation occurred selectively at only one of the methyl groups under the irradiation of blue light. Catalytic oxidation of 2-phenoxy-1-phenylethanol (**1c**), a model for lignin,[26, 69] generated C–C bond cleavage product phenol as the major component. Benzaldehyde and small amounts of benzoic acid were also



**Scheme 4** The substrate scope of the C–H oxygenation mediated by **I** with blue vs. purple/black light irradiation. The yield with blue light (top values) is in blue font while purple/black light is purple. General reaction conditions: 0.4 mmol substrate, 0.02 mmol **I**, 4 mL $CH_3CN$ (or $CD_3CN$), irradiated with 1) blue and 2) purple/black lights at 298 K under aerobic conditions for 24 h. Assay yield determined by $^1H$ NMR spectroscopy with 1,4-dioxane as an internal standard. See Sections VIII and XII of the Supplemental Information. [a] Reaction conditions: 1 atm $CH_4$ (or $C_2H_6$) and $O_2$, 0.01 mmol **I**, 4 mL $CD_3CN$. [b] Turnover numbers (TONs) are based on the concentration of products over the catalyst loading, [product]/[**I**].

observed. Diphenylmethane (**1d**) gave up to 87% yield of benzophenone (**1d-ii**) under purple/black light irradiation. On the other hand, triphenylmethane provided up to 51% yield of the expected alcohol (**1e-i**) under purple/black light irradiation, with further reaction resulting in C–C bond cleavage to afford benzophenone (**1d-ii**). Dihydroanthracene (**1f**) predominantly gave the dual oxidation product 9,10-anthraquinone (**1f-ii**, 83% with purple/black irradiation), which is used in the dye and papermaking industries.

Indane could be oxidized to 1-indanone (**1g-ii**) in 70% yield under purple/black light conditions. The cyclic ether 1,3-dihydroisobenzofuran underwent selective reaction to provide the corresponding lactone **1h-i** in up to 74%, with the remainder of the material further oxidized to the anhydride (**1h-ii**) and its hydrolysis product the diacid (**1h-iii**). Isochromane (**1i**) was chosen to examine the positional selectivity of the oxidation. Interestingly, the selectivity for the benzylic oxidation to the non-benzylic oxidation was ~ 4: 1 under both irradiation conditions. The low chemoselectivity in the isochromane oxidation likely reflects the unselective nature of Cl•.[21, 39-41] The sulfur-containing 2-methylthiophene exhibited low conversion to the expected products (**1j-i** and **1j-ii**), perhaps due to oxidation at the sulfur or heteroaromatic system. Substrates containing a nitrogen atom, such as pyrrolidine and piperidine, showed poor conversions (< 5%) under our catalytic system. The coordination of these substrates to the cerium species may result in the deactivation of the cerium catalyst. The light-mediated C–H oxygenation of cyclic alkanes (**1k–1m**), with stronger C–H bonds [BDE (kcal/mol): 95.6 (**1k**), 99.5 (**1l**), 95.7 (**1m**)],[54, 79, 80] was investigated. The corresponding cyclic ketones were the major products with blue light. The purple/black light combination provided a higher overall yield (i.e., the yield of alcohol + ketone).

The light-mediated activation of light alkanes represents an approach to transforming hydrocarbons, often flared, into valuable chemicals. Under 1 atm total of a mixture of $O_2$ and methane or ethane, the conversion of methane to formic acid and ethane to ethanol, acetaldehyde, and acetic acid was achieved (Scheme 4, Figure 2 and Section VII of the Supplemental Information for details).

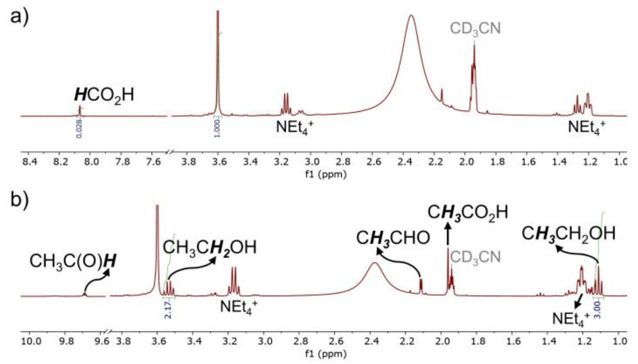


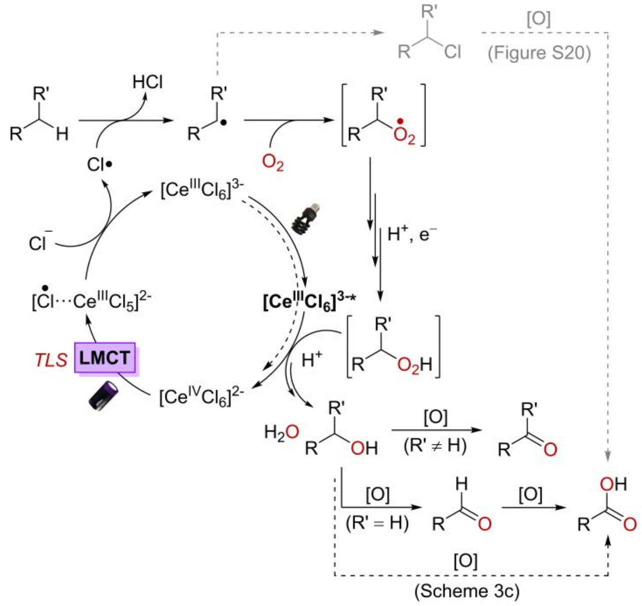
**Fig. 2** $^1H$ NMR spectra of light-mediated C−H oxygenation of (a) $CH_4$ and (b) $C_2H_6$. Reaction conditions: 1 atm $CH_4$ (or $C_2H_6$) and $O_2$, 0.01 mmol **I**, 4 mL $CD_3CN$, irradiated with a Kessil A160WE blue LED lamp at 298 K for 12 h. The quantity of oxidation products was determined using 1,4-dioxane (δ = 3.60 ppm) as an internal standard.

In the case of methane, 4 turn-overs were observed (Figure 2). The limited yield is attributed to the low solubility of methane in acetonitrile at low pressures. The selectivity in the ethane oxygenation was also influenced by light sources: ethanol was observed under blue light irradiation while acetaldehyde and acetic acid were observed under all conditions (Scheme 4, **2b**). An overall 20 turn-overs was observed in ethane activation.

Based on the experiments above and literature precedent, a reaction mechanism for the C−H oxygenation is proposed in Scheme 5. Upon irradiation, $[NEt_4]_2[Ce^{IV}Cl_6]$ undergoes light-induced LMCT and generates Cl•, which is proposed to be the turnover-limiting step. The Cl• undergoes HAT with the substrate C−H bond, producing a carbon-centered radical and hydrogen chloride (HCl). The generated hydrocarbon radical is trapped by $O_2$ to afford the organic superoxide intermediate. Subsequent electron and proton transfer is followed by O−O bond cleavage resulting in oxidized products. It is noteworthy that radical-chain processes are excluded from the proposed mechanism because the quantum yield of the C−H oxygenation (Φ = 1.3%, Section XI of the Supplemental Information) is smaller than that of the photo-induced generation of Cl• from $[NEt_4]_2[Ce^{VI}Cl_6]$ (**I**) (Φ = 1.9%, section XII of the Supplemental Information). The key findings of this work are: oxygen can work as a trapping reagent for different substrates; oxygen is able to regenerate the cerium catalyst in catalytic conditions; black light is involved in the reduction of oxygenated intermediates, presumably by light absorption of the peroxide intermediates or the excitation of $[NEt_4]_3[Ce^{III}Cl_6]$ to generate a stronger reductant $[NEt_4]_3[Ce^{III}Cl_6]^*$. Support for this hypothesis is the change in product distribution in the presence of the dual purple/black light and related control experiments.

## Conclusion

In summary, the light-mediated oxygenation of benzylic and alkane $C(sp^3)$–H bonds is accessible using catalytic $[NEt_4]_2[Ce^{IV}Cl_6]$ under air. A key finding of this work is that the light impacts two reaction stages driven by the catalyst in both reductive and oxidative quenching steps. The selectivity toward more oxidized products increases under irradiation with a purple/black combination of light, which is



**Scheme 5** Proposed catalytic mechanism of C−H oxygenation mediated by $[NEt_4]_2[Ce^{VI}Cl_6]$.

rationalized by the activation of peroxide species under light irradiation. The excited state $[NEt_4]_3[Ce^{III}Cl_6]^*$ (**III**) was proposed to play a role in the activation of the peroxide. The oxidation of benzylic C−H bonds proceeds in good yields. The system also shows reactivity toward cycloalkanes and promising hints of reactivity toward challenging light alkanes (i.e., $CH_4$ and $C_2H_6$) under mild conditions. The influence of radiation wavelengths on the yield and selectivity of C−H oxygenation in this study is expected to prove strategic in optimizing metal-catalyzed light-mediated $C(sp^3)$–H oxidation systems.

## Author Contributions

YHW and QMY optimized the reaction condition, YHW performed substrates screening and characterization, YHW and QMY performed mechanistic studies and drafted the manuscript. EJS and PWJ supervised all aspects.

## Conflicts of interest

There are no conflicts to declare.

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