Supplemental Information

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

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I. General considerations

Dimethylformamide (DMF), dimethoxyethane (DME), and acetonitrile (CH_3CN) were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry Ar and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina or two columns of S3 neutral alumina. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over activated 4 Å molecular sieves for 48 h prior to use. $[NEt_4]_2[Ce^{IV}Cl_6]$ (**I**) was prepared according to a previously published protocol.[1] Other reagents (**1a**−**1m**) were purchased from Fisher Scientific or Sigma-Aldrich and used as received. Methane (99.999%) and ethane (99.999%) were purchased from Matheson Tri-Gas, Inc. and used as received. The photochemical reactions were conducted in 8 mL sample vials with tetrafluoroethylene (TFE) septum under aerobic conditions, irradiated with a) one Kessil A160WE blue light-emitting diode (LED) light or b) one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) compact fluorescence lamps (CFL) ultraviolet A (UVA) light bulbs. The distance between the LED lamps and reaction flasks was 3 cm. The reaction flasks were oven-dried overnight at 150 °C prior to use. The ^1H and ^{13}C NMR spectrum were obtained at 295 K on a Bruker UNI-400 Fourier transform NMR spectrometer with a BBFO probe operating at ^1H frequency of 400 MHz. The data for the ^1H NMR spectrum are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Chemical shifts were recorded in units of parts per million referenced against residual solvent signals (chloroform-d: ^1H (δ = 7.26 ppm), and ^{13}C (δ = 77.16 ppm); acetonitrile-d_3: ^1H (δ = 1.94 ppm), and ^{13}C (δ = 118.26 ppm); dimethyl sulfoxide-d_6: ^1H (δ = 2.50 ppm), and ^{13}C (δ = 39.51 ppm)). Crude mixtures were evaluated by thin-layer chromatography (TLC) using silica gel 60 pre-coated plates (25 mm) and were visualized by UV, I_2, or $KMnO_4$ staining. Flash chromatography was performed with technical grade silica (pore size: 60 Å) as the stationary phase, and all solvents used were of analytical grade.

II. Time course studies of toluene oxygenation

   A. The $[NEt_4]_2[Ce^{IV}Cl_6]$ complex (**I**, 0.0025 mmol, 0.005 M, 5 mol%) was dissolved in 0.5 mL of an air-saturated CD_3CN stock solution containing $PhCH_3$ (0.05 mmol, 0.1 M) and benzene (0.01 mmol, 0.02 M) as an internal standard.[2] The reaction mixture was transferred to a 5 mm O.D. nuclear magnetic resonance (NMR) tube that was subsequently equipped with a stir bar and sealed with a septum. The NMR tube was connected to an air balloon, in which a 6" needle was used to deliver the air from the balloon to the reaction mixture. The needle was pierced through the septum of the NMR tube, as shown in Figure S1. The reaction mixture was stirred on a stir plate with fan cooling and irradiated by one Kessil A160WE blue LED lamp at a distance of 3 cm at 298 K. A cloudy white suspension formed after a 9 h reaction time. The reaction mixture was dark yellow before the reaction started, and it became pale yellow during the course of the reaction.

   Before recording a ^{1}H NMR spectrum each time, the stir bar was removed, and the air balloon was disconnected from the NMR tube. The experimental setup was reverted to its original setting (i.e., Figure S1, with the balloon reattached) each time after recording a ^{1}H NMR spectrum. The conversion of the starting material ($PhCH_3$) and the yield of products for each ^{1}H NMR spectrum (Figure S2) were initially calculated using benzene as an internal standard according to a previously published literature protocol,[2] which was further confirmed with CD_2HCN as a second internal standard, due to the complexity of the aromatic region of the obtained ^{1}H NMR spectrum (see Section II, B for more details).

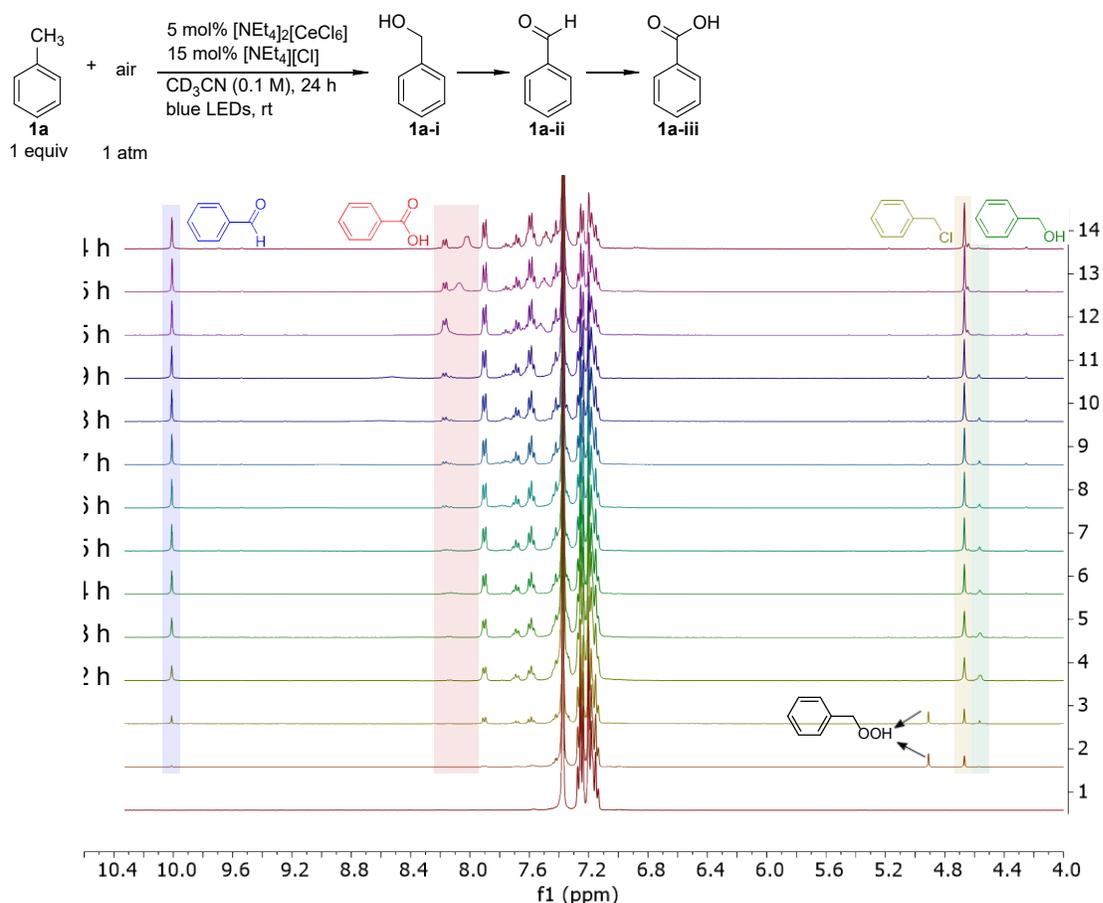**Figure S1.** The experimental setup for the time course studies of toluene oxygenation with ^{1}H NMR spectroscopy.

Figure S2. The stacked ¹H NMR spectrum for the light-mediated toluene oxidation mediated by **I**. The broad peak at δ 7.8–8.0 ppm was presumably due to the formation of a minor amount of cerium-coordinated benzoic acid species.[3] Filtration of the reaction mixture after 24 h reaction through a Celite plug removed this species, as shown in Figure S3. The time-course analysis of various oxidation products is summarized in Figure 1 in the main manuscript. In terms of yield, benzoic anhydride was included in the benzoic products (see Figure S24).
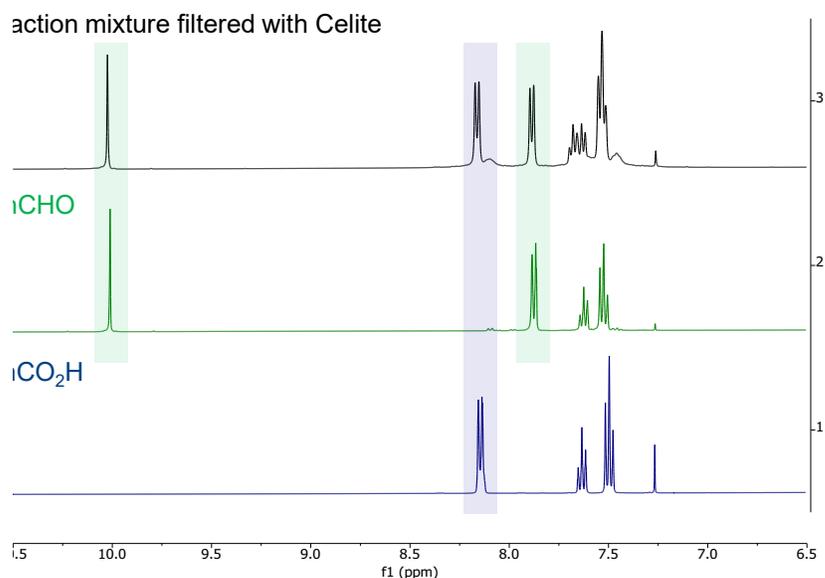
Figure S3. The ^{1}H NMR spectrum of the reaction mixture (a) after filtration through a Celite plug. The ^{1}H spectrum of (b) PhCHO and (c) PhCO$_2$H are listed for the assignment of oxidation products.

B. The residual CD$_2$HCN in the CD$_3$CN solution of the reaction mixture was used as a secondary internal standard to ensure the concentrations of the starting material and products were correctly calculated. A capillary tube filled with CH$_2$Br$_2$ in CD$_3$CN was placed in the NMR tube charged with the reaction mixture (Section II, A) before (t = 0 h) and after (t = 24 h) the toluene oxygenation, respectively (Figure S4). The relative integration value of CH_2Br$_2$ to CD$_2$$H$CN in ^{1}H NMR spectra remained essentially identical before (t = 0 h) and after (t = 24 h) the toluene oxygenation, as revealed in Figure S4 (CH_2Br$_2$:CD$_2$$H$CN = 1: 0.73). This result indicates that catalyst **I** did not activate CD$_2$HCN during the course of the reaction and that CD$_2$HCN could serve as an internal standard for the time course studies of toluene oxygenation with ^{1}H NMR spectroscopy. The time course studies of toluene oxygenation mediated by **I** provided the basis for the plot of the concentration of various species versus time in the main manuscript (cf. Figure 1) are shown in Figure S2.

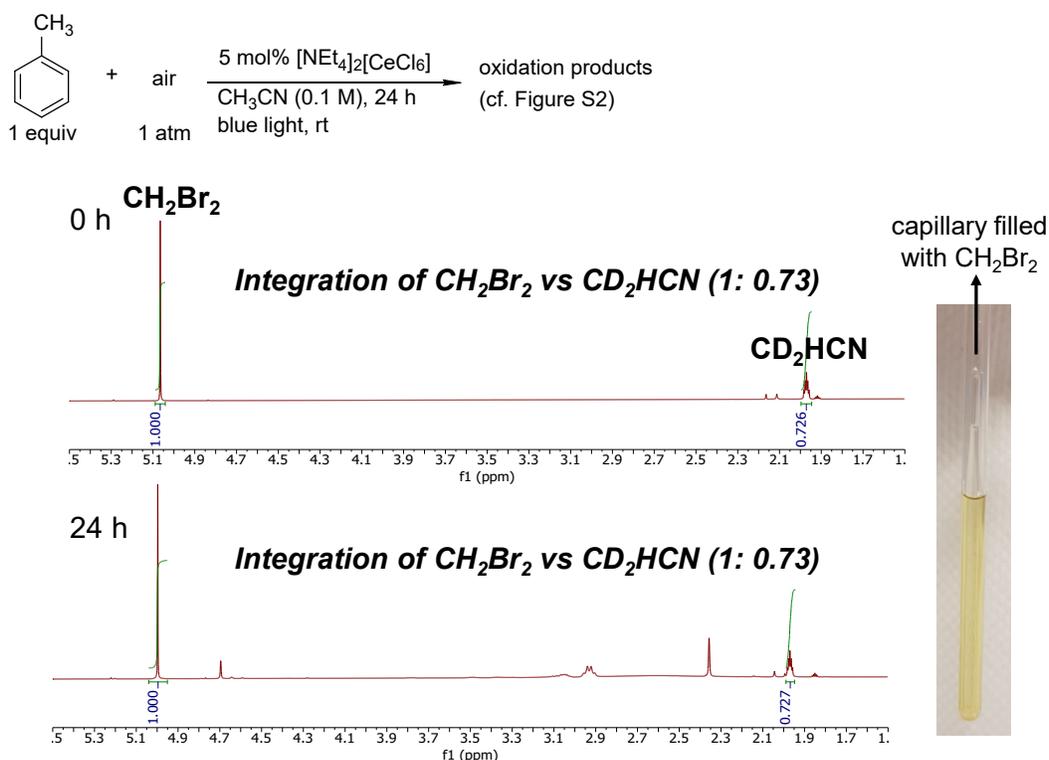**Figure S4.** The ^1H NMR spectrum showed that the relative integration of CH_2Br_2 and CD_2HCN remained unchanged before (a, $t = 0$) and after (b, $t = 24$ h) the toluene oxygenation.

C. The $[NEt_4]_2[Ce^{IV}Cl_6]$ complex (**I**, 0.0025 mmol, 0.005 M, 5 mol%) and *[NEt₄][Cl]* (0.0075 mmol, 0.015 M) were dissolved in 0.5 mL of an air-saturated CD_3CN stock solution containing $PhCH_3$ (0.05 mmol, 0.1 M) and benzene as an internal standard.[4] The reaction mixture was transferred to a 5 mm O.D. NMR tube that was subsequently equipped with a stir bar and sealed with a septum. The NMR tube was connected to an air balloon, in which a 6" needle was used to deliver the air from the balloon to the reaction mixture in the NMR tube. The needle was pierced through the septum of the NMR tube, as shown in Figure S1. The reaction mixture was stirred on a stir plate with fan cooling and irradiated by one Kessil A160WE blue LED lamp at a distance of 3 cm at 298 K. Before recording a ^1H NMR spectrum each time, the stir bar was removed, and the air balloon was disconnected from the NMR tube. The experimental setup was reverted to its original setting (i.e., Figure S1, with the balloon reattached) after recording a ^1H NMR spectrum each time.

The conversion of the starting material ($PhCH_3$) and the yield of products were initially calculated using benzene as an internal standard according to a previously published literature protocol,[2] which was further confirmed with CD_2HCN as a second internal standard due to the complexity of the aromatic region of the obtained ^1H NMR spectrum (Section II, B). Compared to the reaction conditions where the 15 mol% [NEt₄][Cl] was absent (cf. Section II, A, and Figure 1 in the main manuscript), the NMR yield of $PhCHO$ for the conditions including 15 mol% [NEt₄][Cl] was increased from 15% to 32%, and the NMR yield of $PhCO_2H$ was decreased from 18% to 4%. The NMR yield of the byproduct, $PhCH_2Cl$, was slightly increased from 10% to 12% (Figures S5-6).

The ^1H NMR time course studies reveal that the byproduct, $PhCH_2Cl$, was still generated in the presence of [NEt₄][Cl] (15 mol%). It has been reported that the production of $Cl_2^{\cdot-}$ through the

reaction between Cl⁻ and Cl˙ is kinetically favorable,[5] and the reactivity of Cl₂˙⁻ toward C–H activation is lower than that of Cl˙.[6] The production of PhCO₂H by the oxidation of PhCHO is presumably slowed due to the less reactive Cl₂˙⁻ species, in which the Cl₂˙⁻ species was formed by reaction between Cl˙ and Cl⁻ in the presence of 15 mol% [NEt₄][Cl] under these catalytic conditions.[7]
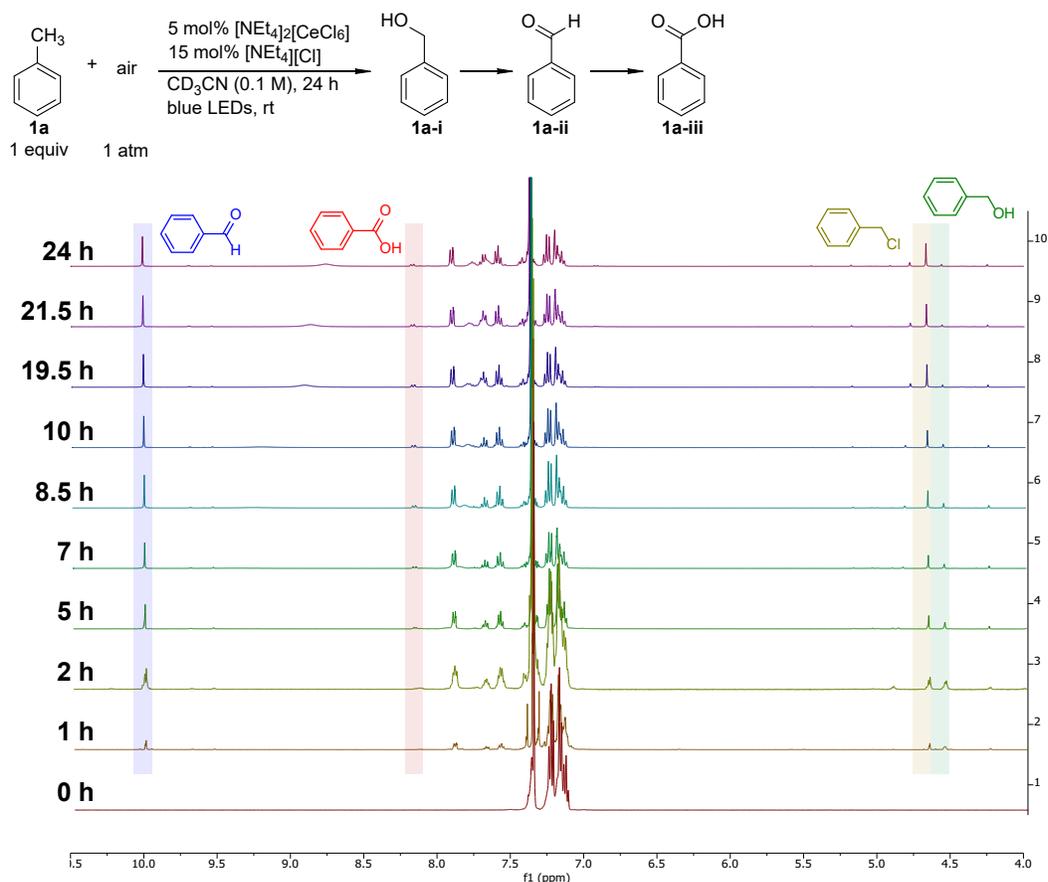

Figure S5. The stacked ¹H NMR spectrum for the light-mediated catalytic toluene oxidation in the presence of *15 mol% [NEt₄][Cl]*.
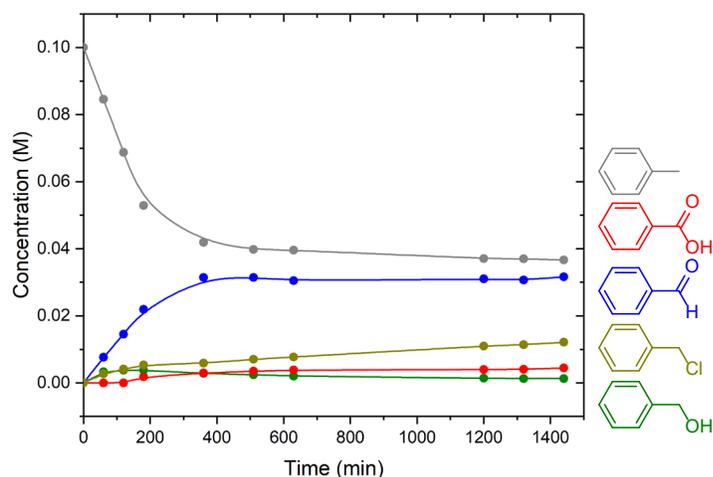
Figure S6. Time course studies on C−H oxygenation of toluene by ^{1}H NMR spectroscopy: distribution of oxidation products. Reaction conditions: 0.1 M toluene, 0.005 M **I** (5 mol%), *0.015 M [NEt$_4$][Cl] (15 mol%)*, 0.5 mL CD$_3$CN in an NMR tube (0.38 mm thickness), irradiated with one Kessil A160WE blue LED lamp at 298 K under aerobic conditions for 24 h.

D. The formation of PhCH$_2$Cl was proposed due to the reaction of benzyl radical (i.e., PhCH$_2$•) with chlorine species (e.g., Cl•, Cl$_2$•⁻) rather than molecular O$_2$, as shown in Figure S7. Control experiments showed that the oxidation of PhCH$_2$Cl to PhCHO and PhCO$_2$H also occurred under catalytic conditions (Section VIII), which released chloride anion back to the reaction mixture and prevented the catalyst from decomposing due to the loss of chloride anions.
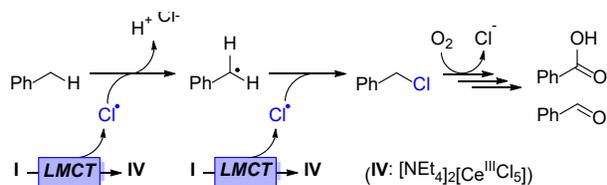

Figure S7. The proposed mechanism for the formation and reaction of PhCH$_2$Cl under catalytic conditions.

III. Light on-off experiments

The [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] complex (**I**, 0.0025 mmol, 0.005 M, 5 mol%) was dissolved in 0.5 mL of an air-saturated CD$_3$CN stock solution containing PhCH$_3$ (0.05 mmol, 0.1 M). The reaction mixture was transferred to a 5 mm O.D. NMR tube that was subsequently equipped with a stir bar and sealed with a septum. The NMR tube was connected to an air gas balloon, in which a 6" needle was used to deliver the air from the balloon to the reaction mixture in the NMR tube. The needle was pierced through the septum of the NMR tube, as shown in Figure S1. The reaction mixture was stirred on a stir plate with fan cooling and irradiated by one Kessil A160WE blue LED lamp at a distance of 3 cm at 298 K.

Before recording a ^{1}H NMR spectrum each time, the stir bar was removed, and the air balloon was disconnected from the NMR tube. The experimental setup was reverted to its original setting (i.e., Figure S1, with the balloon reattached) after recording a ^{1}H NMR spectrum each time. The conversion of the starting material (PhCH$_3$) was determined by the integration of aromatic hydrogens of PhCH$_3$ against the internal standard of CD$_2$HCN. The time-course study of the light switching on-off experiment with consumption of PhCH$_3$ is plotted, as shown in Figure S8. The results confirmed that this is a light-driven reaction consistent with the control experiments shown in Table 1, entries 3-4 in the main manuscript.
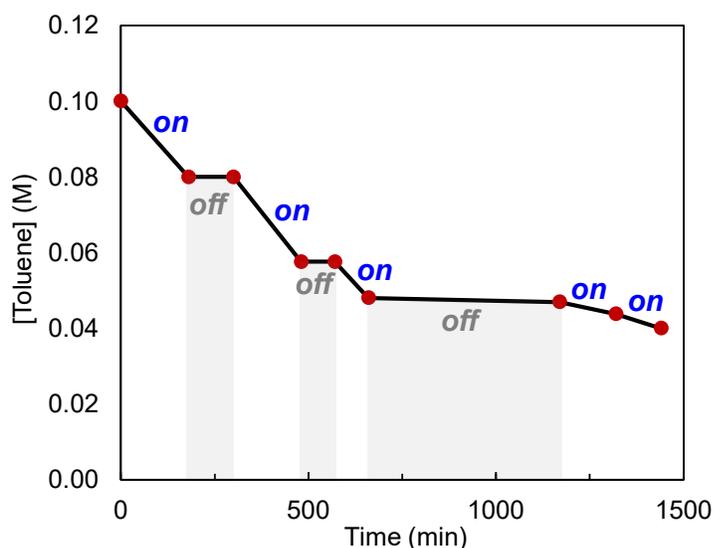

Figure S8. Light on-off experiment with toluene under oxygenation conditions.

IV. Kinetic isotope effect (KIE) studies[8]

A. Two parallel reactions.

The [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] complex (**I**, 0.0025 mmol, 0.005 M, 5 mol%) was dissolved in 0.5 mL of an air-saturated CD$_3$CN stock solution containing PhCH$_3$ (0.05 mmol, 0.1 M) or PhCD$_3$ (0.05 mmol, 0.1 M). The reaction mixture was transferred to a 5 mm O.D. NMR tube that was subsequently equipped with a stir bar and sealed with a septum (Figure S1). The NMR tube was connected to an air gas balloon, in which a 6" needle was used to deliver the air from the balloon to the reaction mixture in the NMR tube. The needle was pierced through the septum of the NMR tube, as shown in Figure S1. The reaction mixture was stirred on a stir plate with fans cooling and irradiated with one Kessil A160WE blue LED lamp at 298 K.

Before recording a ^{1}H NMR spectrum each time, the stir bar was removed, and the air balloon was disconnected from the NMR tube. The experimental setup was reverted to its original setting (i.e., Figure S1) after recording a ^{1}H NMR spectrum each time. The conversion of the starting material (i.e., PhCH$_3$ or PhCD$_3$) was determined by the integration of aromatic hydrogens of PhCH$_3$ or PhCD$_3$ against the internal standard of CD$_2$HCN. The plot of the concentrations of PhCH$_3$ and PhCD$_3$ versus time is shown in Figure S9. The data were fit to the first-order kinetic model with Origin software to estimate the rate constants for the consumption of PhCH$_3$ (k_H) and PhCD$_3$ (k_D). The parallel KIE value (k_H/k_D) was determined from the rate constants of these two parallel reactions.

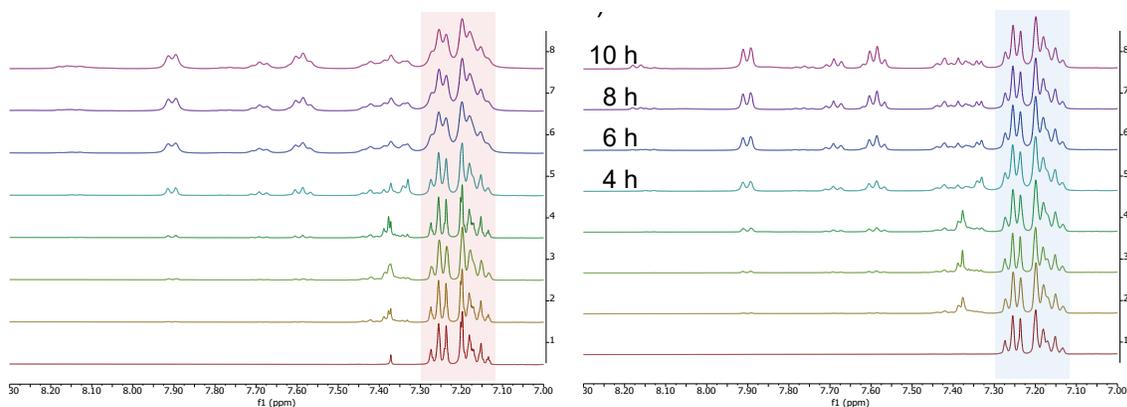**Figure S9.** The ^{1}H NMR spectrum of light-mediated oxygenation of a) PhCD$_3$ and b) PhCH$_3$ in 10 h.

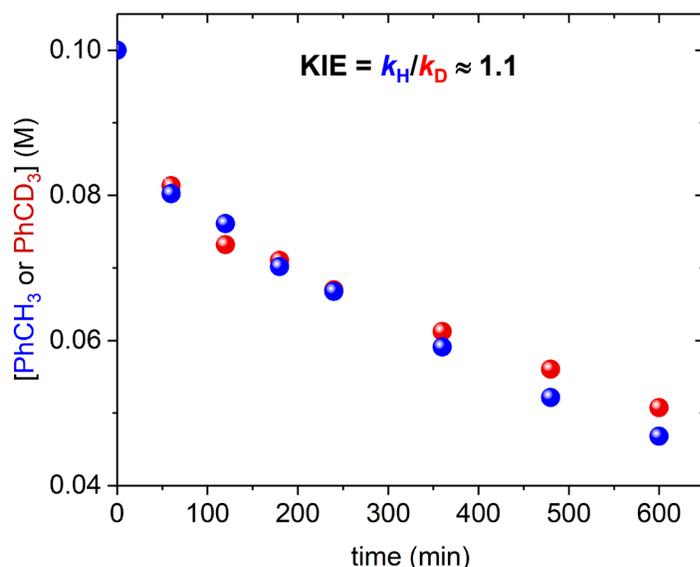| Time (min)\ [substrate] (M)	0	60	120	180	240	360	480	600
[PhCH$_3$]	0.1	0.080	0.076	0.070	0.067	0.059	0.052	0.047
[PhCD$_3$]	0.1	0.081	0.073	0.071	0.067	0.061	0.056	0.051

Figure S10. The parallel KIE for the light-mediated C−H oxygenation of $PhCH_3$ and $PhCD_3$.

B. An intermolecular competition.

In an 8 mL sample vial containing a stir bar, $[NEt_4]_2[Ce^{IV}Cl_6]$ (**I**, 0.01 mmol, 0.005 M, 5 mol%), $PhCH_3$ (0.2 mmol, 0.1 M), and $PhCD_3$ (0.2 mmol, 0.1 M) were dissolved in 2 mL of an air-saturated CD_3CN solvent. The sample vial was subsequently equipped with a stir bar and sealed with a septum, and the septum was pierced with a 16-gauge needle to ensure the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling and irradiated with one Kessil A160WE blue LED lamp at 298 K. After irradiation for 24 h, the reaction mixture was filtered through a Celite plug, and 1,4-dioxane (0.05 mmol) was added to this filtrate as an internal standard to calculate the remaining $PhCH_3$ and $PhCD_3$. The solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^1H NMR spectrum was recorded.

The competitive KIE value was determined from the ratio of the remaining starting materials ($[PhCD_3]/[PhCH_3]$), and the absence of any KIE (1.0) suggests that C−H activation is not the turnover-limiting step in the toluene oxygenation. The remaining $PhCH_3$ concentration was determined by integrating CH_3 and C_6H_5– of Ph–CH_3 against the internal standard of 1,4-dioxane, which was calculated to be 0.154 mmol. The remaining $PhCD_3$ concentration was subsequently derived by subtracting the integration of all aromatic hydrogens from that of aromatic hydrogens of $PhCH_3$, which was calculated to be 0.156 mmol.
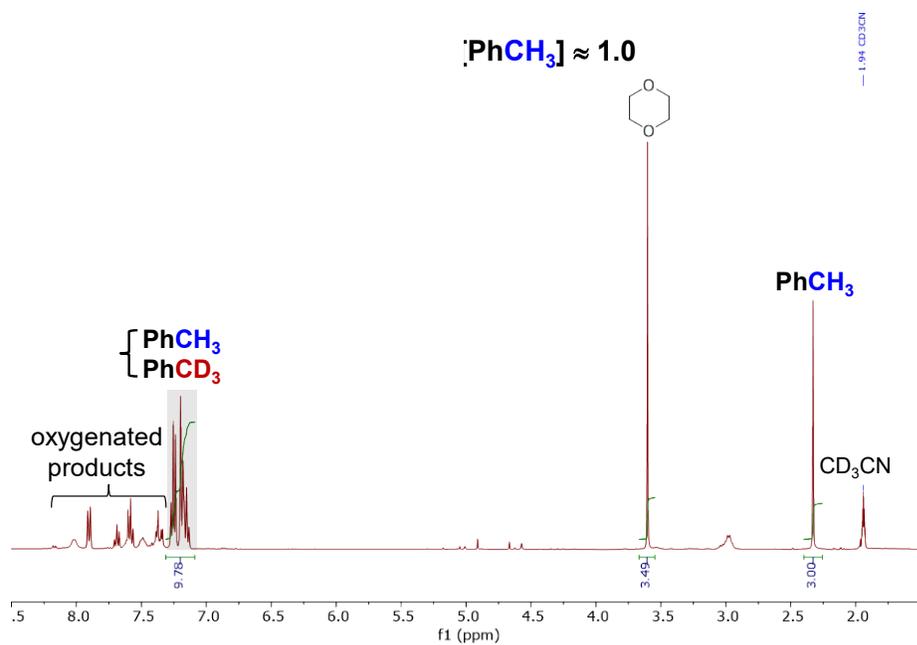
Figure S11. The competitive KIE for the light-mediated C-H oxygenation of PhCH$_3$ and PhCD$_3$.

V. UV-visible spectrum of $[NEt_4]_2[Ce^{IV}Cl_6]$

  The UV-visible spectrum of **I** (0.2 mM) in CH_3CN was recorded at 298 K, and the wavelength of maximum visible absorption was approximately 380 nm, as shown in Figure S10.[9] The UV-visible spectrum of complex **I** suggest that the light emitted from Kessil PR160-390 LED lamps[10] was more efficiently absorbed by **I** than Kessil A160WE blue LED lamps.[11] This outcome provides a rationale for higher conversions and yields of C–H oxygenation (Scheme 5 in the main manuscript) because the generation of Cl• via LMCT of **I** is proposed to be the turnover-limiting step (Scheme 2 in the main manuscript).
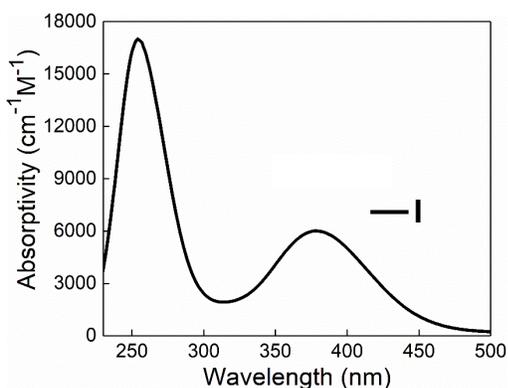
Figure S12. The UV-visible spectrum of **I** was recorded in CH_3CN at 298 K.

VI. Light-mediated C−H oxygenation under different light irradiations

A. Irradiation with a blue LED lamp.

The setup for the reactions irradiated with one Kessil A160WE blue LED lamp is shown in Figure S13. The distance between the blue LED lamp and the reaction vessels (i.e., 8 mL sample vials) was 3 cm.

Figure S13. The setup for the photochemical oxygenation of arenes and alkanes under irradiation with one Kessil A160WE blue LED lamp.

B. Irradiation with a purple LED lamp and four UVA light bulbs.

The setup for the reaction irradiated with one Kessil PR160-390 LED lamp and four UVA light bulbs are shown in Figure S14. The distance between the purple LED lamp, and the reaction vessels (i.e., 8 mL sample vials) was 5 cm. The reaction vessels were surrounded by four 24 W (100 W equivalent) CFL UVA light bulbs, which were 3 cm away from the reaction vessels.
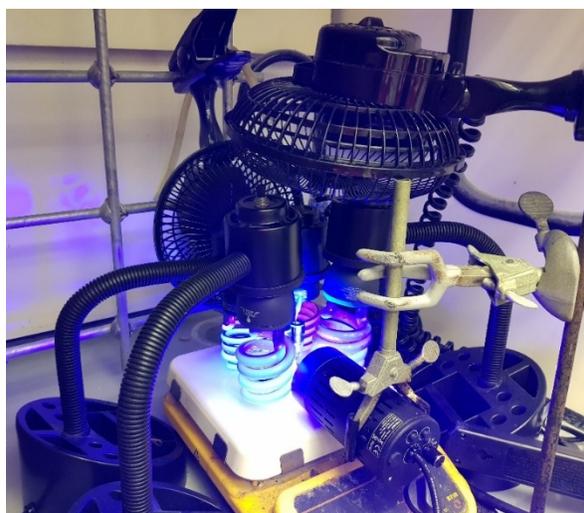
Figure S14. The setup for photochemical oxygenation of hydrocarbons under irradiation with one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs.

VII. Light-mediated C−H oxygenation of light alkanes (CH₄ and C₂H₆)

In a 4 mL sample vial, the $[NEt_4]_2[Ce^{IV}Cl_6]$ complex (**I**, 0.01 mmol, 0.0025 M, 5 mol%) was initially dissolved in 4 mL anhydrous CD_3CN, and the CD_3CN solution of **I** was vigorously sparged with CH_4 (or C_2H_6) for 5 min. The reaction mixture was subsequently transferred to an 8 mL sample vial with a TFE septum, and the sample vial was connected to a balloon filled with O_2 and a balloon filled with CH_4 (or C_2H_6). The reaction mixture was stirred on a stir plate with fan cooling at 298 K and irradiated by a) one Kessil A160WE blue LED lamp, and b) one Kessil PR160-390 LED lamp, and four 24 W (100 W equivalent) CFL UVA light bulbs (Figure S18).

$$CH_4 \text{ or } C_2H_6 + O_2 \xrightarrow[\substack{CD_3CN, \text{ rt, 12 h} \\ \textbf{\textit{different lights}}}]{5 \text{ mol\% } [NEt_4]_2[CeCl_6]} \text{oxidation products}$$
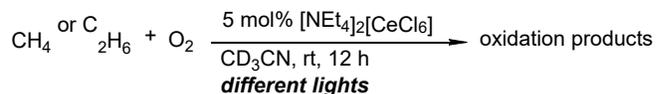
Figure S15. The setup for photochemical oxygenation of CH_4 and C_2H_6 under one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs.

The reaction was stopped after 12 h by turning off the lights, and the reaction mixture was filtered through a Celite plug. 1,4-Dioxane (0.05 mmol) was added to each solution as an internal standard. The solution was subsequently transferred to a 5 mm O.D. NMR tube and the ¹H NMR spectrum were recorded. The respective yields of oxidation products were determined by the integration of each product against the internal standard (1,4-dioxane), as shown in Table 3 in the main manuscript. The ¹H NMR is contained in the manuscript, and the ¹³C spectrum is below.
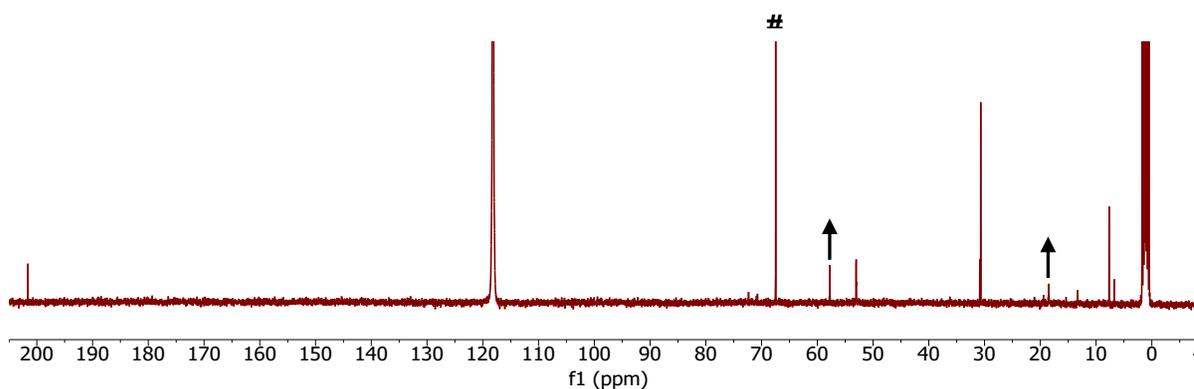
Figure S16. The ^{13}C NMR spectrum of the crude product of the light-mediated ethane oxygenation. The spectrum was recorded in CD_3CN, and the peak indicated by # is the internal standard of 1,4-dioxane. For the corresponding ^1H NMR spectrum, see Figure 2b in the main manuscript.

VIII. Control experiments of light-mediated C–H oxygenation for toluene derivative, benzyl chloride, benzyl alcohol, and acetic acid

A. *Light-mediated oxidation using a combination of purple/UVA lights.*

We next wanted to investigate the influence of radiation wavelengths on C−H oxygenation and determine if the combination of purple/UVA lights (Section VII, B) leads to improved reactivity. The complex $[NEt_4]_2[Ce^{IV}Cl_6]$ (**I**, 0.01 mmol, 0.005 M, 5 mol%) was dissolved in 2 mL of an air-saturated CD_3CN solution containing *p*-tolunitrile (0.2 mmol, 0.1 M). The reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K and irradiated with a) one Kessil A160WE blue LED lamp, and b) one Kessil PR160-390 LED lamp, and four 24 W (100 W equivalent) CFL UVA light bulbs. The reaction was stopped after 24 h by turning off the lights, and the reaction mixture was filtered through a Celite plug. 1,4-Dioxane (0.05 mmol) was added to this solution as an internal standard. The solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^1H NMR spectrum were recorded (Figure S21). Their respective yields of PhCHO and $PhCO_2H$ were determined by the integration against the internal standard of 1,4-dioxane. Under irradiation with one Kessil A160WE blue LED lamp, only 4-formylbenzonitrile (37%) was detected (Figure S21a). The production of 4-cyanobenzoic acid (21%) was observed when the reaction was irradiated with one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs (Figure S21b).

Figure S17. The ^{1}H NMR spectra of these experiments revealed that *p*-tolunitrile could be oxidized to 4-cyanobenzoic acid under irradiation with a combination of purple LED and UVA lights.

B. *Light-mediated oxidation of PhCH₂Cl to PhCHO and/or PhCO₂H.*

The formation of PhCH$_2$Cl was observed for C−H oxygenation of toluene (Figure 1 in the main manuscript and Figure S2). This product was found to be further oxidized to PhCO$_2$H under the catalytic conditions of toluene oxygenation, although the oxidation rate of PhCH$_2$Cl to PhCO$_2$H was sluggish. The [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] complex (**I**, 0.02 mmol, 0.005 M, 5 mol%) was dissolved in 4 mL of an air-saturated CD$_3$CN solution containing PhCH$_2$Cl (0.4 mmol, 0.1 M). The reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K and irradiated by a) one Kessil A160WE blue LED lamp, and, separately, b) one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs. The reaction was stopped after 24 h, and the crude solution was filtered through a Celite plug. 1,4-Dioxane (0.05 mmol) was added to this solution as an internal standard. The solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^{1}H NMR spectrum were recorded (Figure S20). Their respective yields of PhCHO and PhCO$_2$H were determined by the integration against the internal standard of 1,4-dioxane. The production of PhCHO (4%) and PhCO$_2$H (4%) was observed when the reaction was irradiated with one Kessil A160WE blue LED lamp (Figure S20a). Under irradiation with one Kessil PR160-

390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs, the NMR yield of $PhCO_2H$ was 12%, but there was no appreciable yield of PhCHO (Figure S20b). The conversion of $PhCH_2Cl$ was calculated to be a) 15% and b) 20% under these catalytically relevant conditions.
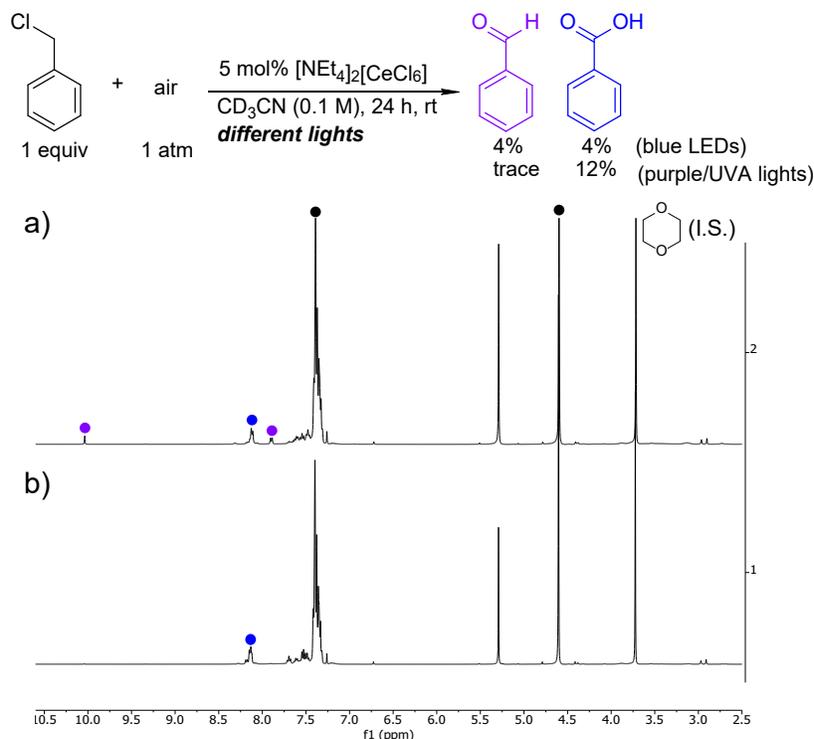
Figure S18. The ^1H NMR spectrum of the reactions described above indicates that the oxidation of $PhCH_2Cl$ to PhCHO and/or $PhCO_2H$ occurred under the catalytic conditions of toluene oxygenation (cf. Figure 1 in the main manuscript). The result presented in Figure S20 indicates that the reaction was influenced by radiation wavelengths.

C. Probing the reaction of $PhCH_2OH$ with air and $[NEt_4]_2[Ce^{IV}Cl_6]$ in the absence of light.

The oxidation of $PhCH_2OH$ is a light-driven reaction, which was confirmed by a controlled experiment (Figure S22). The $[NEt_4]_2[Ce^{IV}Cl_6]$ complex (**I**, 0.02 mmol, 0.005 M, 5 mol%) was dissolved in 4 mL of an air-saturated CH_3CN solution containing $PhCH_2OH$ (0.4 mmol, 0.1 M). The reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K in the dark. The reaction was stopped after 24 h, and the crude solution was placed on a rotary evaporator to remove CH_3CN. This crude mixture was dissolved in 5 mL CH_2Cl_2, filtered through a Celite plug, and the filtrate was subsequently placed on a rotary evaporator to remove CH_2Cl_2. The concentrated crude product was dissolved in $CDCl_3$, and 1,4-dioxane (0.05 mmol) was added to the solution as an internal standard. The $CDCl_3$ solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^1H NMR spectrum was recorded. The yield of PhCHO was determined by the integration against the internal standard of 1,4-dioxane, but the negligible conversion of $PhCH_2OH$ to PhCHO was observed, as shown in Figure S19.
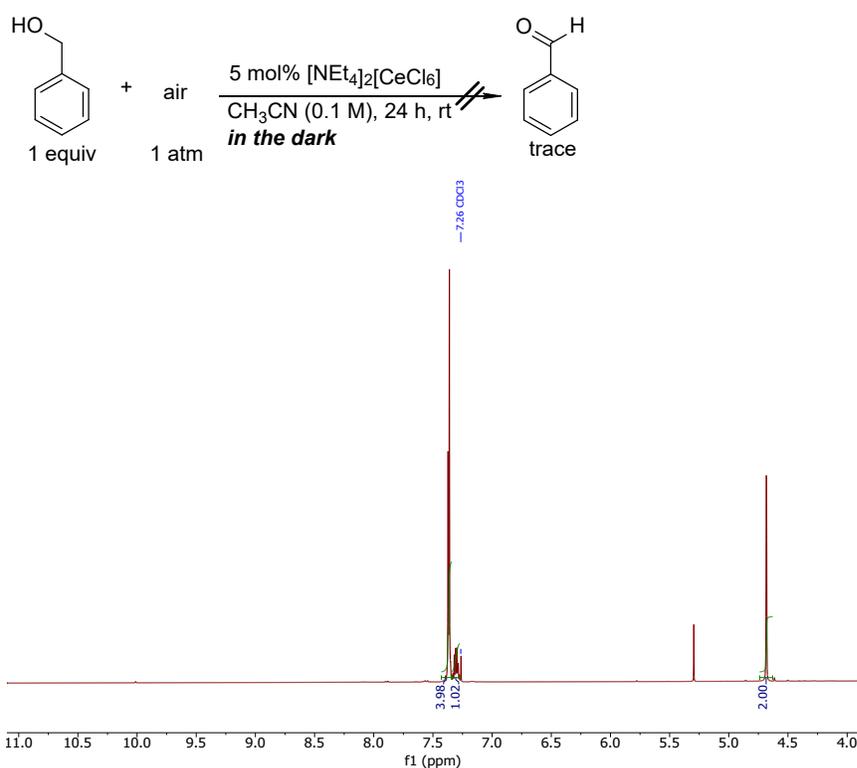
Figure S19. The ^{1}H NMR spectrum showed that the conversion of PhCH$_2$OH to PhCHO was negligible in the dark.

D. Probing the reaction of PhCH$_2$OH with air and [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] with different light. See Scheme 3a. Similar conditions for toluene activation were used.

E. Negligible oxidation of HCO$_2$H to CO$_{2(g)}$ and H$_{2(g)}$.

To investigate the oxidation of HCO$_2$H to CO$_2$ and H$_2$ under our reaction conditions, HCO$_2$H was used as a substrate. First, [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] (**I**, 0.01 mmol, 0.005 M, 5 mol%) was dissolved in 2 mL of an air-saturated CD$_3$CN containing HCO$_2$H (0.2 mmol, 0.1 M), and a stir bar was added. Next, the reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure the reaction was performed under aerobic conditions. Next, the reaction mixture was stirred on a stir plate with fan cooling and irradiated with one Kessil A160WE blue LED lamp at 298 K. The reaction was stopped after 24 h, and the crude solution was filtered through a Celite plug. Next, 1,4-Dioxane (0.05 mmol) was added to this solution as an internal standard. The solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^{1}H NMR spectrum was recorded (Figure S23). The amount of remaining HCO$_2$H was determined by the integration against the internal standard of 1,4-dioxane, which was calculated to be 0.19 mmol (97% left). This result indicates that the oxidation of HCO$_2$H to CO$_2$ and H$_2$ by **I** was negligible under catalytically relevant conditions.
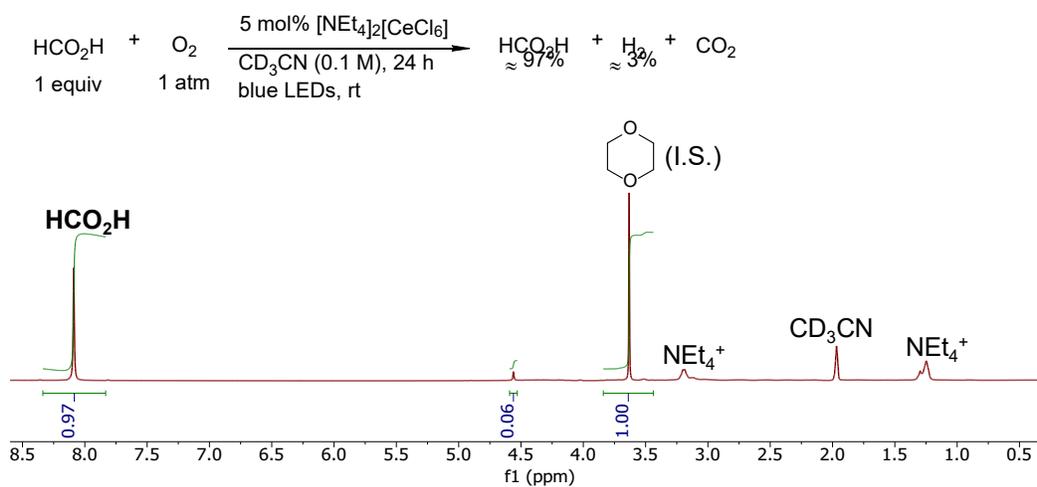
Figure S20. The ^1H NMR spectrum suggests that the oxidation of HCO_2H to CO_2 and H_2 was negligible under catalytic conditions.

IX. Control experiments of light-mediated oxygenation using benzaldehyde

A. Benzaldehyde with toluene under UVA irradiation

A dry CD_3CN (0.844 g/mL) stock solution was moved out from the glovebox and air-saturated. Reagents were added into the 0.50 g stock solution, including $PhCH_3$ (6.3 μL, 0.059 mmol, 0.1 M), PhCHO (2.4 μL, 0.024 mmol, 0.04 M) and 0.5 mg NEt_4Cl (0.5 mg, 0.003 mmol, 0.005 M) as an internal standard. 0.5 mL stock solution was transferred into a 5 mm O.D. nuclear magnetic resonance (NMR) tube that was subsequently equipped with a stir bar and sealed with a septum. The NMR tube was connected to an air balloon, in which a 6" needle was used to deliver the air from the balloon to the reaction mixture. The needle was pierced through the septum of the NMR tube, same as shown in Figure S1. The reaction mixture was stirred on a stir plate with fan cooling and irradiated by 4 UVA lamps at a distance of 3 cm at 298 K. Before recording a ^{1}H NMR spectrum each time, the stir bar was removed, and the air balloon was disconnected from the NMR tube. The experimental setup was reverted to its original setting (i.e., same as Figure S1, with the balloon reattached) each time after recording a ^{1}H NMR spectrum. A time-course experiment was performed to monitor whether toluene can be activated using benzaldehyde as a triplet photosensitizer. The conversion of the substrate (i.e., $PhCH_3$), the consumption of the photosensitizer (i.e., PhCHO), and the yield of products for each ^{1}H NMR spectrum were calculated using $[NEt_4][Cl]$ as an internal standard at each time point (Figure S24), including the beginning of the reaction (0 h). $[NEt_4][Cl]$ was regarded as innocent in this reaction, consistent with the lack of its activation product in the ^{1}H NMR spectra.

The amount of $PhCH_3$ has decreased about 20% at 24 h, primarily due to evaporation. Because a decrease in the overall integration of aromatic protons (e.g., δ 6–9 ppm) is similar to the depletion of $PhCH_3$ at 24 h in the aromatic region in ^{1}H-NMR (Figure S24 and Table S1). The overall equivalents of benzyl aldehyde, benzoic acid, and benzoic anhydride did not change much either (9.4 equiv at 0 h and 9.6 equiv at 24 h). The result shows that only a negligible amount of $PhCH_3$ was converted to oxidation products, besides the evaporation of $PhCH_3$.

The most significant reaction was the conversion of benzaldehyde to benzoic acid and benzoic anhydride. As a result, 7.3 equiv benzaldehyde was consumed, and 5.5 equiv benzoic acid and 1.0 equiv benzoic anhydride (from 2 equiv of benzaldehyde) was generated at 24 h. It is known that benzaldehyde can be photoexcited, and its excited triplet states can do various reactions, including Norrish type I and Norrish type II reactions.[12] However, in our cases, with the existence of oxygen, none of the Norrish I type products were observed, including benzene, benzyl alcohol, benzoin, and benzil. The absence of the activation products was rationalized by the quenching/sensitization of excited benzaldehyde with ground state triplet oxygen. In the case of sensitization, the excited singlet oxygen was known to facilitate the oxidation of benzaldehyde.[13]

In addition to the major reaction of benzyl aldehyde oxidation, there are very few activation products of $PhCH_3$ being observed in the reaction, such as $PhCH_2OH$ (0.2 equiv was observed at its highest yield at 36 h) and $PhCH_2OOH$ (0.2 equiv was observed at its highest yield at 36 h). No $PhCH_2Cl$ was observed during the reaction.
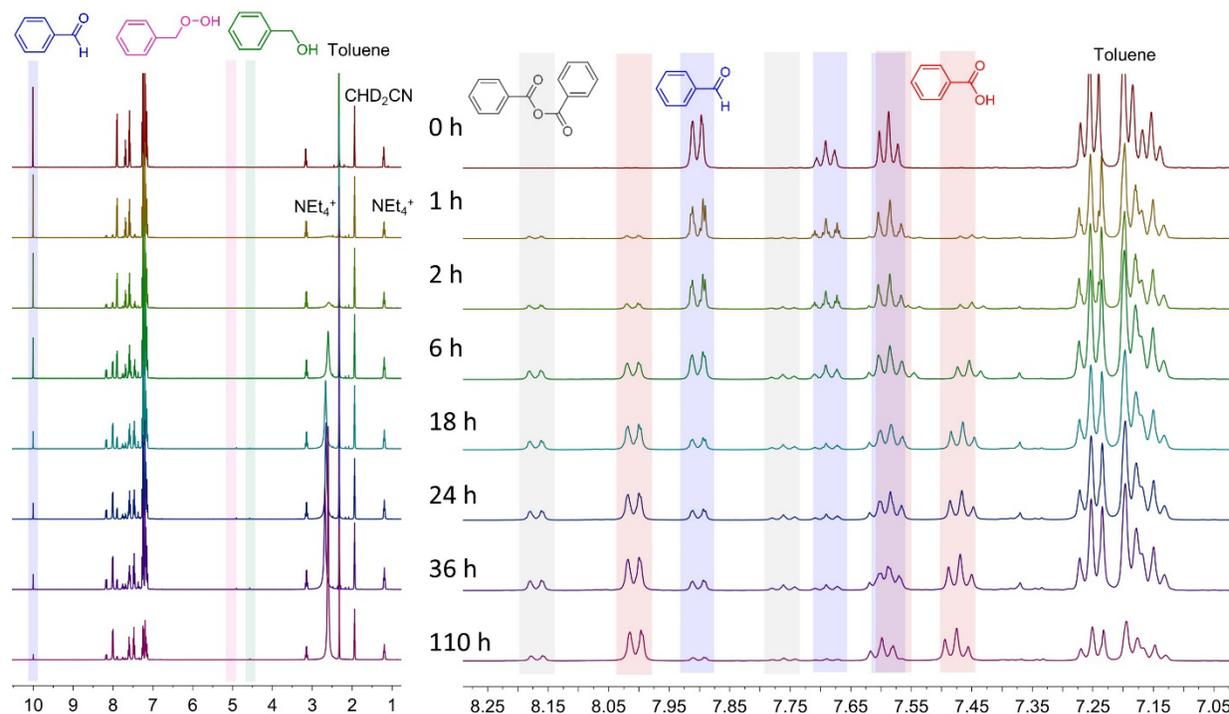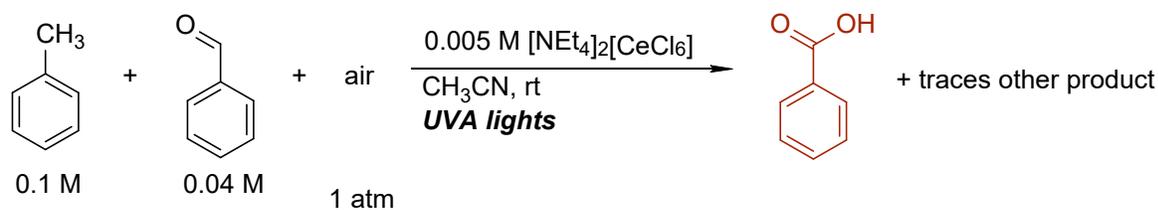
Figure S21. The stacked ^{1}H NMR spectrum for the control experiment with toluene and benzaldehyde under UVA irradiation. The time-course analysis of various oxidation products is summarized in Table S1.

Table S1. The control experiment of toluene oxygenation using benzaldehyde under the irradiation of UVA light

Time/Equiv[a]	Toluene[b]	Benzyl aldehyde[c]	Benzoic acid[d]	Benzoic Anhydride[e]	All[f]
0 h	22.4	9.2	0.2	0.0	31.8
1 h	21.9	7.6	0.9	0.3	30.3
2 h	21.4	6.6	1.5	0.5	29.9
6 h	20.2	4.4	3.3	0.8	29.8
18 h	18.3	2.2	5.4	1.0	28.7
24 h	17.1	1.9	5.7	1.0	27.6
36 h	16.1	1.6	6.0	0.9	26.6

| 110 h | 8.7 | 0.8 | 7.4 | 0.6 | 18.6 |

[a]Equivalents were calculated with NEt$_4$Cl as an internal standard; toluene: 0.1 M and benzyl aldehyde: 0.04 M as starting material; [b] toluene equivalents are based on methyl peak; [c]benzyl aldehyde equivalents are based on $-$C(O)H peak; [d]benzoic acid equivalents were based on peak around 8 ppm; [e]benzoic anhydride equivalents were based on peak around 8.1-8.2 ppm, each equiv of benzoic anhydride contains 2 equiv of benzoic acids; [f]overall equivalents are based on integration over 6-9 ppm, divide by five hydrogen atoms per molecule in aromatic region.

B. Oxidation of PhCHO in the absence of light with catalyst I

The oxidation of PhCHO to PhCO$_2$H was found to occur in the absence of light (Figure S23). The [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] complex (I, 0.02 mmol, 0.005 M, 5 mol%) was dissolved in 4 mL of an air-saturated CH$_3$CN solution containing PhCHO (0.4 mmol, 0.1 M) and a stir bar. The reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction was performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K in the dark. The reaction was stopped after 24 h, and the reaction mixture was placed on a rotary evaporator to remove CH$_3$CN. This crude product was dissolved in 5 mL CH$_2$Cl$_2$ and filtered through a Celite plug, and the filtrate was subsequently placed on a rotary evaporator to remove CH$_2$Cl$_2$. The concentrated crude product was dissolved in CDCl$_3$, and 1,4-dioxane (0.05 mmol) was added to the solution as an internal standard. The CDCl$_3$ solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^{1}H NMR spectrum was recorded. The yield of PhCHO was determined by the integration against the internal standard of 1,4-dioxane, which was calculated to be 39% (Figure S23).

Since benzaldehyde was not converted to benzoic acid without catalyst I in the air or converted very slow, adding catalyst I could help with the oxidation of benzaldehyde in the absence of light irradiation under aerobic conditions. Although this control experiment showed that the oxidation of benzaldehyde (1a-ii) to benzylic acid (1a-iii) by [NEt$_4$]$_2$[CeCl$_6$] could occur in the absence of light irradiation, the yield is approximately 20% (TON = 8) lower than that of in the presence of light irradiation (cf. Scheme 3b, TON = 13 (purple/black lights) and TON = 12 (blue light)). Most importantly, the oxidation of benzyl alcohol to benzaldehyde does not occur in the absence of catalyst I under light irradiation, suggesting that catalyst I plays an essential role in the catalytic system. The mechanistic studies of thermal oxidation of 1a-ii to 1a-iii by [NEt$_4$]$_2$[CeCl$_6$] under aerobic conditions are still under investigation.
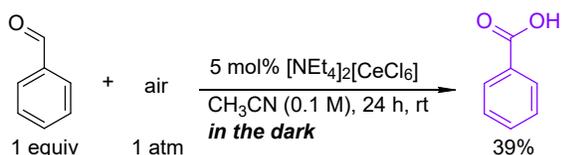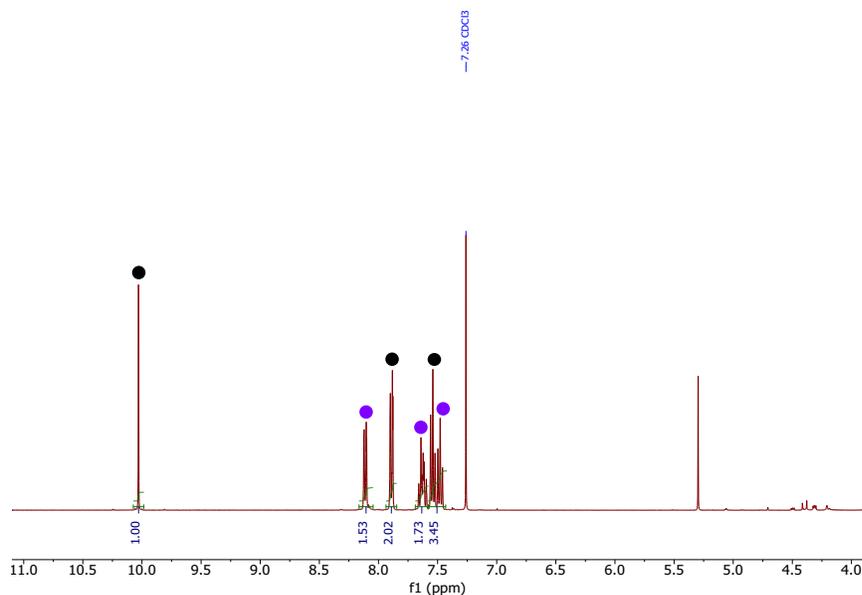
Figure S22. The ^1H NMR spectrum showed that the oxidation of PhCHO to PhCO$_2$H was mediated by **I** in the dark under the reaction conditions.

C. Catalytic oxidation of PhCHO with catalyst **I** using different light sources (Scheme 3b)

starting from PhCHO (**1a-ii**)

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

The [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] complex (**I**, 0.02 mmol, 0.005 M, 5 mol%) was dissolved in 4 mL of an air-saturated CH$_3$CN solution containing PhCHO (0.4 mmol, 0.1 M) and a stir bar. The reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction was performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K and irradiated with a) one Kessil A160WE blue LED lamp (Figure S13), and separately, b) one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs (Figure S14). The reaction was stopped after 24 h, and the reaction mixture was placed on a rotary evaporator to remove the volatile material. The resulting crude mixture was dissolved in 5 mL CH$_2$Cl$_2$, filtered through a Celite plug, and the filtrate placed on a rotary evaporator to remove CH$_2$Cl$_2$. The concentrated crude product was dissolved in CDCl$_3$, and 1,4-dioxane (0.05 mmol) was added to the solution as an internal standard. The CDCl$_3$ solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^1H NMR spectrum was recorded. The yields of PhCO$_2$H under the irradiation of different light sources were determined by the integration against the internal standard of 1,4-dioxane, which are calculated to be 61% (one Kessil A160WE blue LED lamp) and 64% (one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs), respectively (Scheme 3b).

The experiments illustrated in Section X, C and Scheme 3b in the main manuscript reveal that the oxidation of $PhCH_2OH$ to PhCHO was more susceptible to radiation wavelengths. However, the influence of different radiation wavelengths on the oxidation of PhCHO to $PhCO_2H$ is insignificant (cf. Scheme 3b and relevant discussion in the main manuscript) because this reaction could proceed by **I** in the absence of light irradiation. Combined with the oxidation of benzaldehyde under UVA light, with catalyst **I** in the absence of light irradiation, and with catalyst **I** under different light sources (cf. Scheme 3c), we can conclude that multiple factors are facilitating the oxidation of benzaldehyde under aerobic conditions. Using different light source give similar conversion rate of benzaldehyde to benzoic acid, indicating that with compound **I**, benzaldehyde excited states make a minor contribution to its oxidation. On the other hand, UVA makes a more significant difference in the oxidation of benzyl alcohol (Scheme 3a), indicating the influence of cerium(III) excited states (i.e., *J. Am. Chem. Soc.* **2016,** *138,* 16266–16273) and intermediate peroxide oxidation (Scheme 3c and Section VII).

X. Control experiment of light-mediated O–O bond cleavage of PhC(CH$_3$)$_2$OOH

A stable alkyl hydroperoxide, PhC(CH$_3$)$_2$OOH (80% solution in C$_6$H$_6$), was selected to investigate the influence of radiation wavelengths on the light-mediated O–O bond cleavage of alkyl hydroperoxides mediated by [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] (i.e., Scheme 3c in the main manuscript). In an 8 mL sample vial containing a stir bar, [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] (**I**, 0.01 mmol, 0.005 M, 5 mol%) and PhC(CH$_3$)$_2$OOH (0.2 mmol, 0.1 M) were dissolved in 2 mL of an air-saturated CD$_3$CN solvent. The sample vial was subsequently equipped with a stir bar and sealed with a septum, and the septum was pierced with a 16-gauge needle to ensure the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling and irradiated with (a) one Kessil PR160-390 LED lamp and four 24 W CFL UVA light bulbs (Figure S15), (b) one Kessil A160WE blue LED lamp (Figure S16), and (c) four 24 W CFL UVA light bulbs (Figure S17). After irradiation for 24 h, each reaction mixture was filtered through a Celite plug, and 1,4-dioxane (0.05 mmol) was added to each filtrate as an internal standard to calculate the NMR yield of PhC(CH$_3$)$_2$OH. Each solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^{1}H NMR spectrum was recorded.

The observation of PhC(CH$_3$)$_2$OH under the irradiation of various light, together with controlled experiments that the yield of PhC(CH$_3$)$_2$OH was less than 10% in the absence of light irradiation, suggesting that the O–O bond cleavage of PhC(CH$_3$)$_2$OOH occurred under photochemical conditions. Although the production of PhC(CH$_3$)$_2$OH occurred under the light irradiation in the absence of complex **I**, a considerable increase of the yield was obtained in the presence of 5 mol% **I**. These outcomes indicate that **I** was involved in the O–O bond cleavage of PhC(CH$_3$)$_2$OOH under photochemical conditions. The dual irradiation of purple/black lights (Figure S15) affords the highest yield of PhC(CH$_3$)$_2$OH, among other radiation wavelengths. The effect of black light on the O–O bond cleavage of PhC(CH$_3$)$_2$OOH is similar to that of blue light (Figures S16-17). These results are rationalized that a highly reducing intermediate **III** was formed under the irradiation of black light, facilitating the O–O bond cleavage of PhC(CH$_3$)$_2$OOH.
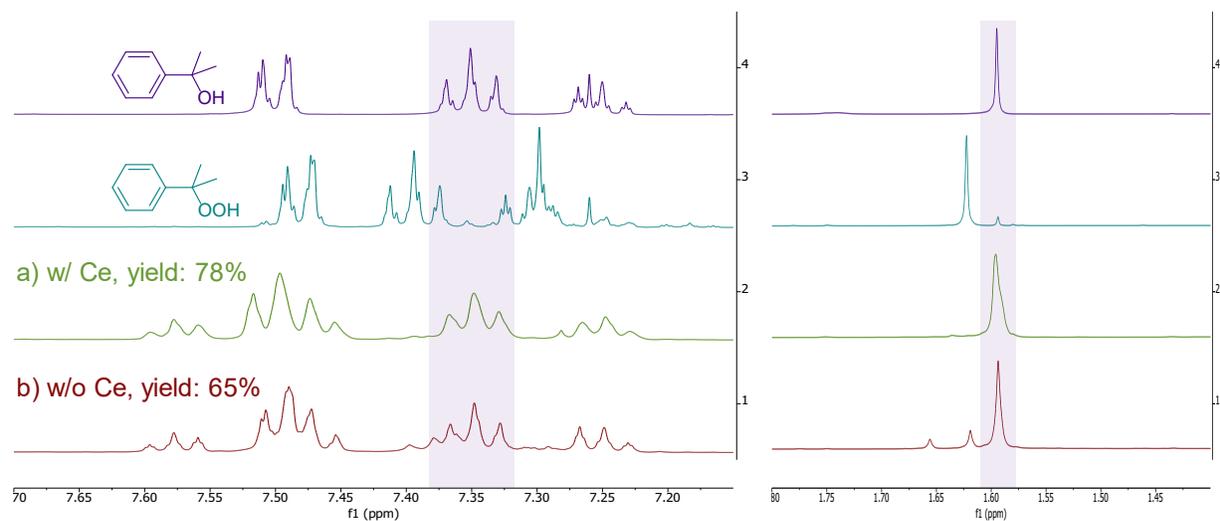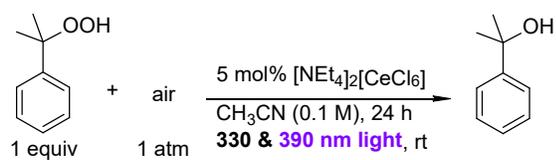
Figure S23. Light-mediated conversion of PhC(CH$_3$)$_2$OOH to PhC(CH$_3$)$_2$OH under the dual irradiation of purple and black lights (see also Figure S14 for the experimental setup). (a) The NMR yield of PhC(CH$_3$)$_2$OH was 78% in the presence of 5 mol% **I**. (b) The NMR yield of PhC(CH$_3$)$_2$OH was 65% in the absence of **I**.
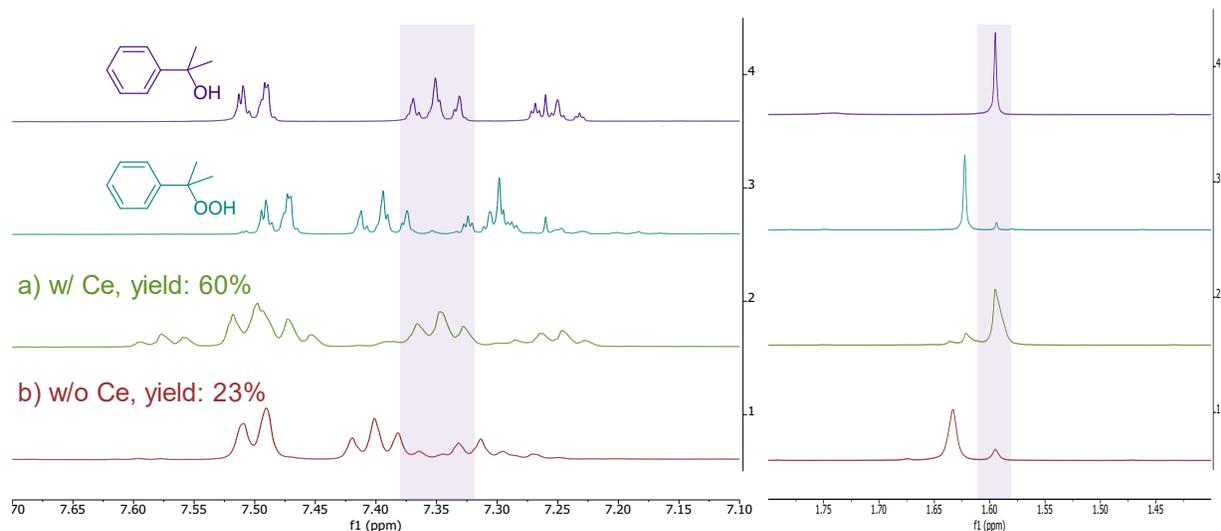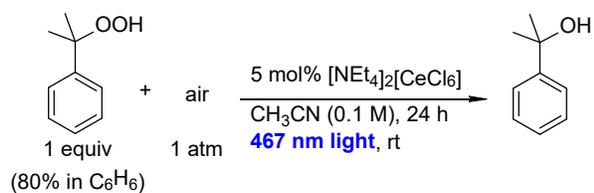
Figure S24. Light-mediated conversion of $PhC(CH_3)_2OOH$ to $PhC(CH_3)_2OH$ under the irradiation of blue light (see also Figure S13 for the experimental setup). (a) The NMR yield of $PhC(CH_3)_2OH$ was 60% in the presence of 5 mol% **I**. (b) The NMR yield of $PhC(CH_3)_2OH$ was 23% in the absence of **I**.
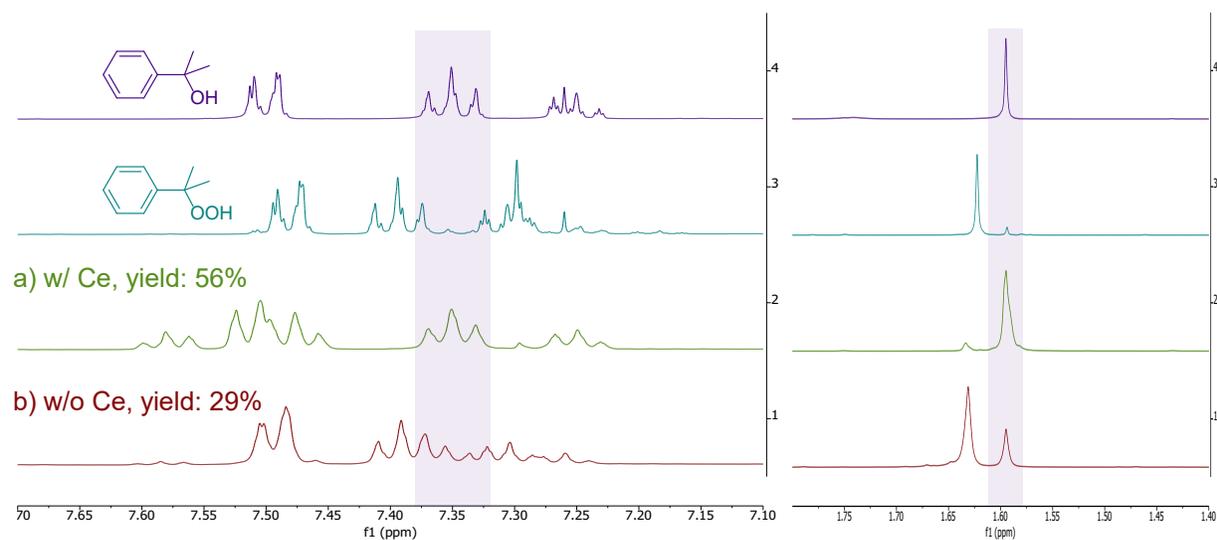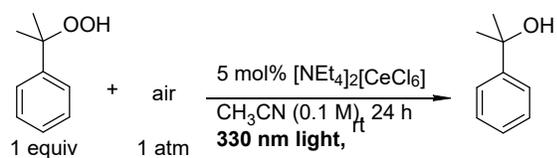
Figure S25. Light-mediated conversion of PhC(CH$_3$)$_2$OOH to PhC(CH$_3$)$_2$OH under the irradiation of black light. The experimental setup is similar to that of Figure S14 but without the Kessil PR160-390 LED lamp. (a) The NMR yield of PhC(CH$_3$)$_2$OH was 56% in the presence of 5 mol% **I**. (b) The NMR yield of PhC(CH$_3$)$_2$OH was 29% in the absence of **I**.

XI. Quantum yield measurement: C−H oxygenation

A. *Determination of the light intensity at 467 nm.*

The photon flux of one Kessil A160WE blue LED lamp was determined by standard ferrioxalate actinometry.[14] A 0.15 M solution of ferrioxalate was prepared by dissolving 1.8115 g of potassium ferrioxalate hydrate in 25 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 51.8 mg of phenanthroline and 11.71 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. These two solutions were stored in the dark. A volume of 4 mL of the ferrioxalate solution was added to an 8 mL sample vial with a TFE septum and a stir bar. The reaction was stirred and irradiated for 5 s with one Kessil A160WE blue LED lamp. After irradiation, 1 mL of this irradiated ferrioxalate solution, 17.00 mL of phenanthroline (phen) buffer solution, and 82.00 mL deionized water were added to a 100 mL volumetric flask with a stirring bar. The solution was stirred for 1 h to allow the ferrous ions to coordinate to the phenanthroline completely. The absorbance of the solution was measured at 510 nm with UV-visible spectroscopy. A non-irradiated sample was also prepared, and the absorbance at 510 nm was measured with UV-visible spectroscopy. The conversion of ferrous ions was calculated to be 1.25×10^{-5} mol using eq 1. In eq 1, V is the total volume of the solution (4 mL). This solution was diluted by 100 times after the addition of phenanthroline and deionized water, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated ferrous solutions (0.3459, the mean of three independent experiments), l is the path length (1 cm), and ε is the molar absorptivity of $Fe(phen)_3^{2+}$ at 510 nm ($11,100$ L mol^{-1} cm^{-1}).[14a]

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} \qquad \text{(eq 1)}$$

The photon flux of one Kessil A160WE blue LED lamp at 467 nm was calculated using eq 2. $\Phi_{Fe^{2+}}$ is the quantum yield for the ferrioxalate actinometer ($\Phi_{Fe^{2+}} = 1.01$),[14a] t is the irradiated time (5 s), and f ($f = 1 - 10^{-\text{Absorbance (Abs)}}$) is the fraction of light absorbed at $\lambda = 467$ nm ($f > 0.999$ because Abs > 2). The photon flux was calculated to be 2.48×10^{-6} einstein s^{-1}, based on the mean of three independent experiments.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi_{Fe^{2+}} \times t \times f} \qquad \text{(eq 2)}$$

B. *Determination of the reaction quantum yield.*

In an 8 mL sample vial containing a stir bar, $[NEt_4]_2[Ce^{IV}Cl_6]$ (**I**, 0.02 mmol, 0.005 M, 5 mol%) and $PhCH_3$ (0.4 mmol, 0.1 M) were dissolved in 4 mL air-saturated CD_3CN. The sample was capped with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction was performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling and irradiated with one Kessil A160WE blue LEDs at 298 K. The reaction was stopped after 1800 s, and the solution was filtered through a Celite plug. 1,4-Dioxane (0.05 mmol) was added to this filtrate as an internal standard. The solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^1H NMR spectrum was recorded to determine the yield. The quantum yield of toluene oxygenation was determined using eq 3. Essentially, all

incident light ($f > 0.999$) was absorbed by **I** under the reaction conditions described above. A total of 9.20×10^{-6} mol product (14% yield) was generated in 1800 s. Therefore, the reaction quantum yield was calculated to be 1.3%.

$$\Phi_{rxn} = \frac{\text{mol product}}{\text{flux} \times t \times f} \qquad\qquad \text{(eq 3)}$$

XII. Quantum yield measurement: generation of Cl• from [NEt$_4$]$_2$[Ce^{IV}Cl$_6$]

A. *Determination of the light intensity at 467 nm.*
The procedure is identical to that of Section XI.A.

B. *Determination of the reaction quantum yield*.
The photon flux of one Kessil A160WE blue LED lamp was determined by standard ferrioxalate actinometry. [NEt$_4$]$_2$[Ce^{IV}Cl$_6$] (**I**, 0.125 mmol, 0.005 M, 5 mol%) was dissolved in 25 mL of an N$_2$-saturated stock solution of CH$_3$CN. Then, 4.00 mL of this stock solution was added to an 8 mL sample vial containing a stir bar under anaerobic conditions. The solution was irradiated for 45 s with one Kessil A160WE blue LED lamp. After irradiation, the solution was diluted by a factor of 20 using CH$_3$CN, and the absorbance of the diluted solution at 378 nm was measured with UV-visible spectroscopy. Conversion of **I** was calculated using Beer-Lambert Law ($\Delta A = \varepsilon \times l \times \Delta c$), where ΔA is the difference in absorbance at 378 nm between the irradiated and non-irradiated solutions of **I** (0.1518, the mean of three independent experiments), ε is the molar absorptivity of **I** at 378 nm (5,630 L mol^{-1} cm^{-1}),[9a] l is the path length (1 cm), and Δc is the difference in concentration of the diluted solution of **I** (2.70×10^{-5} M).

The conversion of **I** was calculated to be 2.16×10^{-6} mol (mol = 2.70×10^{-5} M $\times$ 4 mL $\times$ 20 (20 times dilution)). The quantum yield of photoreduction of **I** was determined using eq 3. Essentially, all incident light ($f > 0.999$ because Abs > 3) was absorbed by **I** under the reaction conditions described above, t is the irradiated time (45 s), and photon flux is defined as the mol of photons per second (2.48×10^{-6} mol s^{-1}). Therefore, the reaction quantum yield was calculated to be 1.9%.

XIII. General procedures for light-mediated C−H oxygenation of hydrocarbons

A. General Procedure I.
[NEt$_4$]$_2$[Ce^{IV}Cl$_6$] (**I**, 0.02 mmol, 0.005 M, 5 mol%) was dissolved in 4 mL of an air-saturated CH$_3$CN stock solution containing a hydrocarbon substrate (0.4 mmol, 0.1 M). The reaction mixture was transferred to an 8 mL sample vial with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure that the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K and irradiated with a) one Kessil A160WE blue LED lamp (Figure S13), and separately, b) one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs (Figure S14). The reaction was stopped after 24 h, and the reaction mixture was placed on a rotary evaporator to remove the volatile material. The resulting crude mixture was dissolved in 5 mL CH$_2$Cl$_2$, filtered through a Celite plug, and the filtrate placed on a rotary evaporator to remove CH$_2$Cl$_2$. The concentrated crude product was dissolved in CDCl$_3$, and 1,4-dioxane (0.05 mmol) was added to the solution as an internal

standard. The CDCl₃ solution was subsequently transferred to a 5 mm O.D. NMR tube and the ^{1}H NMR spectrum was recorded to determine the yield. The crude product was purified by flash chromatography on silica gel using mixtures of ethyl acetate and hexanes as the mobile phase.

B. General Procedure II.

[NEt₄]₂[Ce^{IV}Cl₆] (**I**, 0.02 mmol, 0.005 M, 5 mol%) was dissolved in 4 mL of an air-saturated CD₃CN stock solution containing a hydrocarbon substrate (0.4 mmol, 0.1 M). The reaction mixture was transferred to an 8 mL sample vial fitted with a TFE septum, and the septum was pierced with a 16-gauge needle to ensure the reaction could be performed under aerobic conditions. The reaction mixture was stirred on a stir plate with fan cooling at 298 K and irradiated with a) one Kessil A160WE blue LED lamp (Figure S13), and, separately, b) one Kessil PR160-390 LED lamp and four 24 W (100 W equivalent) CFL UVA light bulbs (Figure S14). The reaction was stopped after 24 h, and the crude solution was filtered through a Celite plug. 1,4-Dioxane (0.05 mmol) was added to this solution as an internal standard. The solution was transferred to a 5 mm O.D. NMR tube and the ^{1}H NMR spectrum was recorded to determine the yield. *General procedure I* refers to the reaction conducted in CH₃CN, and general *procedure II* refers to the reaction conducted in CD₃CN. The crude product was purified by flash chromatography on silica gel using mixtures of ethyl acetate and hexane as the mobile phase.

XIV. Product isolation and characterization
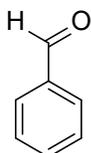
1) Benzaldehyde (**1a-ii**). The crude product of **1a-ii** was obtained following the general procedure II-a (10.2 mg, 5% **1a-iii** impurities was left based on NMR integration, 23% yield). **1a-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl₃): δ 10.01 (s, 1H), 7.89–7.50 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, CDCl₃): δ 192.5, 136.5, 134.6, 129.9, 129.1. The NMR spectral data were consistent with those available in the literature (*Org. Lett.* **2005,** *7,* 3689-3692).
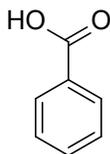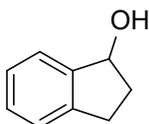

2) Benzoic acid (**1a-iii**). The crude product of **1a-iii** was obtained following the general procedure II-b (29 mg, 59% yield). **1a-iii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl₃): δ 8.15–7.47 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, CDCl₃): δ 172.6, 134.0, 130.3, 129.5, 128.6. NMR spectral data were consistent with those available in the literature (*J. Org. Chem.* **2006,** *71,* 7618-7631).
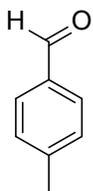
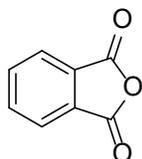3) 4-Methylbenzaldehyde (**1b-i**). The crude product of **1b-i** was obtained following the general procedure II-b (8 mg, 17% yield). **1b-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.96 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 192.1, 145.7, 134.3, 130.0, 129.9, 22.0. NMR spectral data were consistent with those available in the literature (*Org. Lett.* **2005,** *7,* 3689-3692).
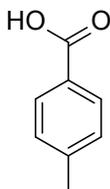
4) 4-Formylbenzoic acid (**1b-ii**). The crude product of **1b-ii** was obtained following the general procedure II-b (21 mg, 39%). **1b-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 172.1, 144.8, 130.4, 129.4, 126.7, 21.9. NMR spectral data were consistent with those available in the literature (*Org. Lett.* **2011,** *13,* 4164-4167).
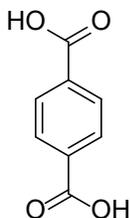
5) Terephthalic acid (**1b-iii**). The crude product of **1b-iii** was obtained following the general procedure II-b (10 mg, 15% yield). **1b-iii** was purified by silica gel flash column chromatography (MeCN: CH$_2$Cl$_2$ = 10: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.29 (s, 2H) 8.04 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 167.1, 134.9, 129.9. NMR spectral data were consistent with those available in the literature (*J. Mol. Catal. Chem.* **2007,** *266,* 139-148).
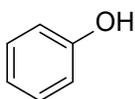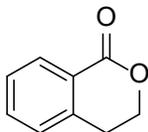
6) Phenol (**1c-i**). The crude product of **1c-i** was obtained following the general procedure II-b (12 mg, 31% yield). **1c-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 10: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29–6.85 (m, 5H), 5.31 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 155.4, 129.8, 121.0, 115.5. NMR spectral data were consistent with those available in the literature (*Organometallics* **2005,** *24,* 4528-4542).
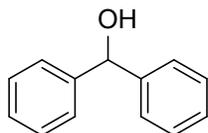
7) Diphenylmethanol (**1d-i**). The crude product of **1d-i** was obtained following the general procedure I-a (8 mg, 31% yield). **1d-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40–7.37 (m, 4H), 7.36–7.32 (m, 4H); 7.29–7.25 (m, 2H), 5.86 (d, *J* = 4.0 Hz, 1H), 2.21 (m, *J* = 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 143.8, 128.5, 127.6, 126.6, 76.3. NMR spectral data were consistent with those available in the literature (*J. Org. Chem.* **2008,** *73,* 1597-1600).
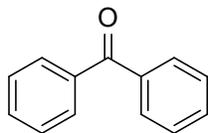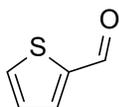

8) Benzophenone (**1d-ii**). The crude product of **1d-ii** was obtained following the general procedure I-b (63 mg, 87% yield). **1d-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82–7.80 (m, 4H), 7.62–7.57 (m, 2H), 7.51–7.47 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 196.9, 137.8, 132.6, 130.2, 128.4. NMR spectral data were consistent with those available in the literature (*Synlett* **2011,** *4*, 559-564).
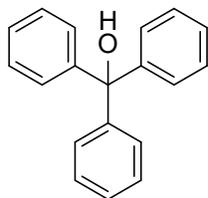
9) Triphenylmethanol (**1e-i**). The crude product of **1e-i** was obtained following the general procedure I-b (53 mg, 51% yield). **1e-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34–7.25 (m, 15H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 147.0, 128.1, 128.1, 127.4, 82.2. NMR spectral data were consistent with those available in the literature (*Chem.: Eur. J.* **2009,** *157*, 6569-6572).
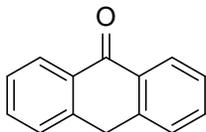
10) 9(10H)-Anthracenone (**1f-i**). The crude product of **1f-i** was obtained following the general procedure I-a (8 mg, 7% 1f-ii impurities, 9% yield). **1f-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a pale yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.39–8.36 (m, 2H), 7.63–7.59 (m, 2H), 7.50–7.47 (m, 4H), 4.38 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 184.4, 140.6, 132.9, 132.2, 128.61, 127.8, 127.2, 32.5. NMR spectral data were consistent with those available in the literature (*Synlett* **2011,** *10*, 1435-1438).
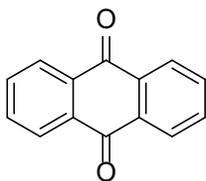
11) 9,10-Anthracenedione (**1f-ii**). The crude product of **1f-ii** was obtained following the general procedure I-b (69 mg, 83% yield). **1f-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a pale yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.33–8.31 (m, 4H), 7.82–7.80 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 183.3, 143.3, 133.7, 127.4. NMR spectral data were consistent with those available in the literature (*Adv. Synth. Catal.* **2011,** *353*, 401-410).
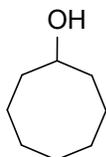

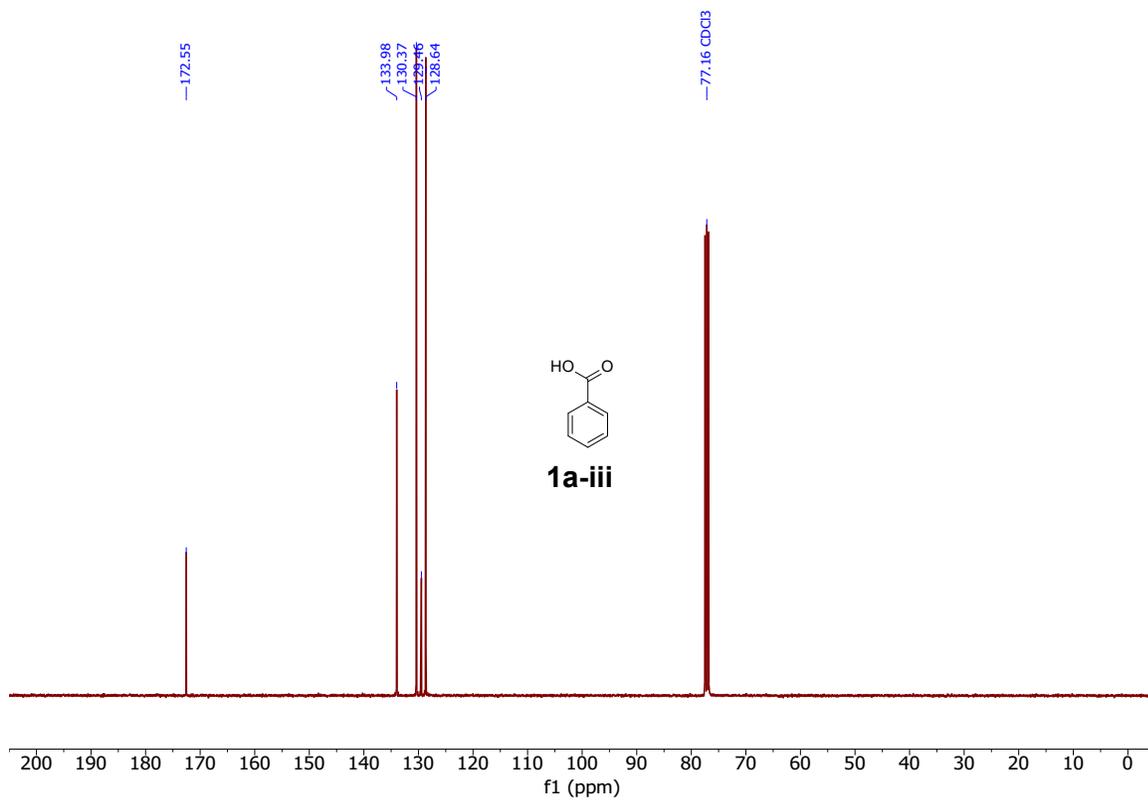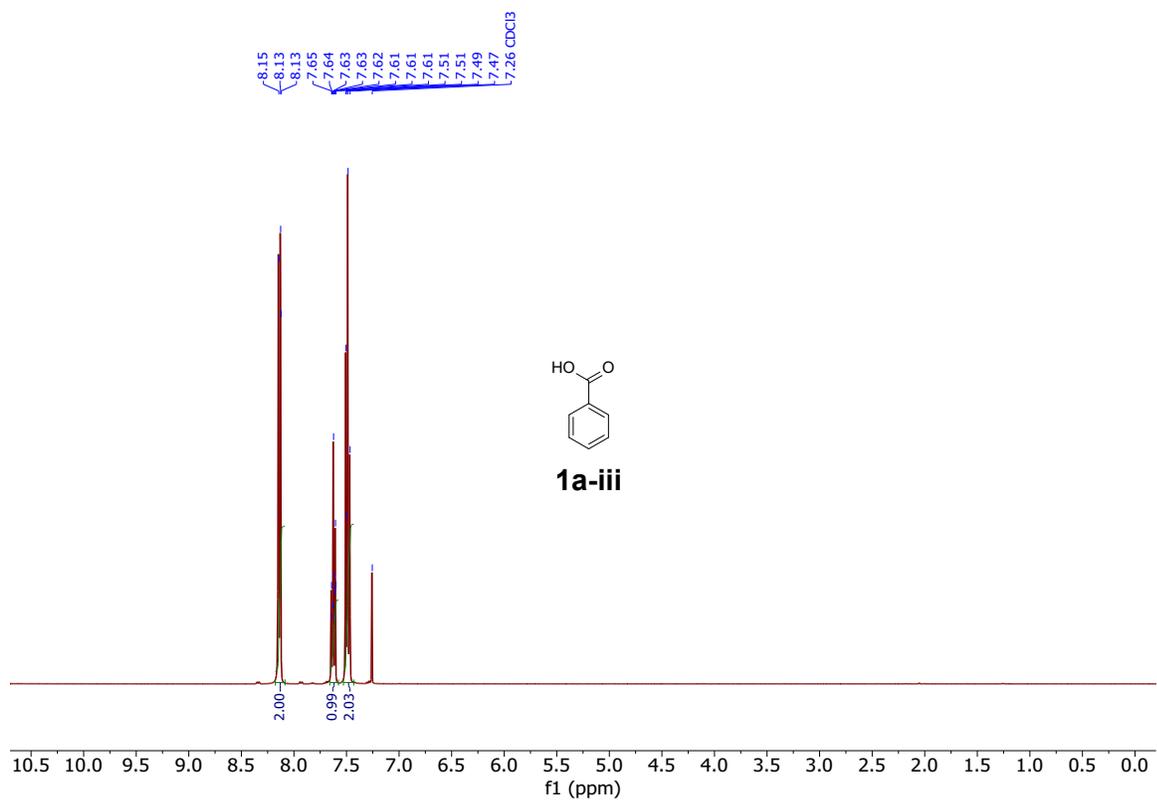12) 1-Indanol (**1g-i**). The crude product of **1g-i** was obtained following the general procedure I-a (10 mg based on the collection of five trials, 14% average yield). **1g-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43–7.41 (m, 1H), 7.27–7.24 (m, 3H), 5.25 (m, 1H), 3.10–3.03 (m, 1H), 2.87–2.79 (m, 1H), 2.54–2.46 (m, 1H), 2.00–1.91 (m, 1H), 1.75–1.73 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 145.1, 143.5, 128.5, 126.9, 125.1, 124.3, 76.7, 36.1, 29.9. NMR spectral data were consistent with those available in the literature (*J. Org. Chem.* **2006,** *71*, 3952-3958).
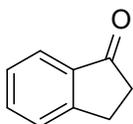
13) 1-indanone (**1g-ii**). The crude product of **1g-ii** was obtained following the general procedure I-b (37 mg, 70% yield). **1g-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, *J* = 8.0 Hz,

1H), 7.58 (t, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 3.14 (t, J = 4.0 Hz, 2H), 2.68 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$): δ 207.2, 155.3, 137.2, 134.7, 127.4, 126.8, 123.8, 36.3, 25.9. NMR data were consistent with those available in the literature (*Adv. Synth. Catal.* **2011,** *353*, 401-410).
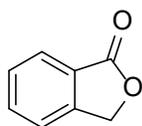
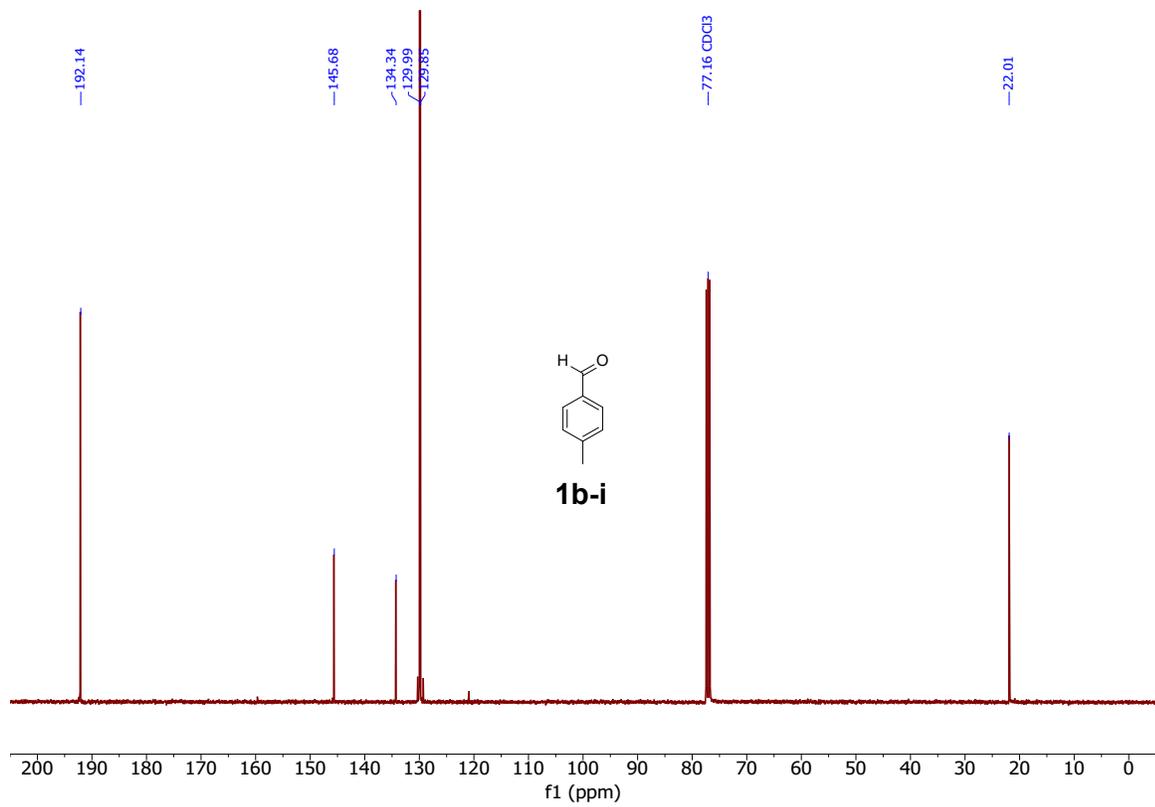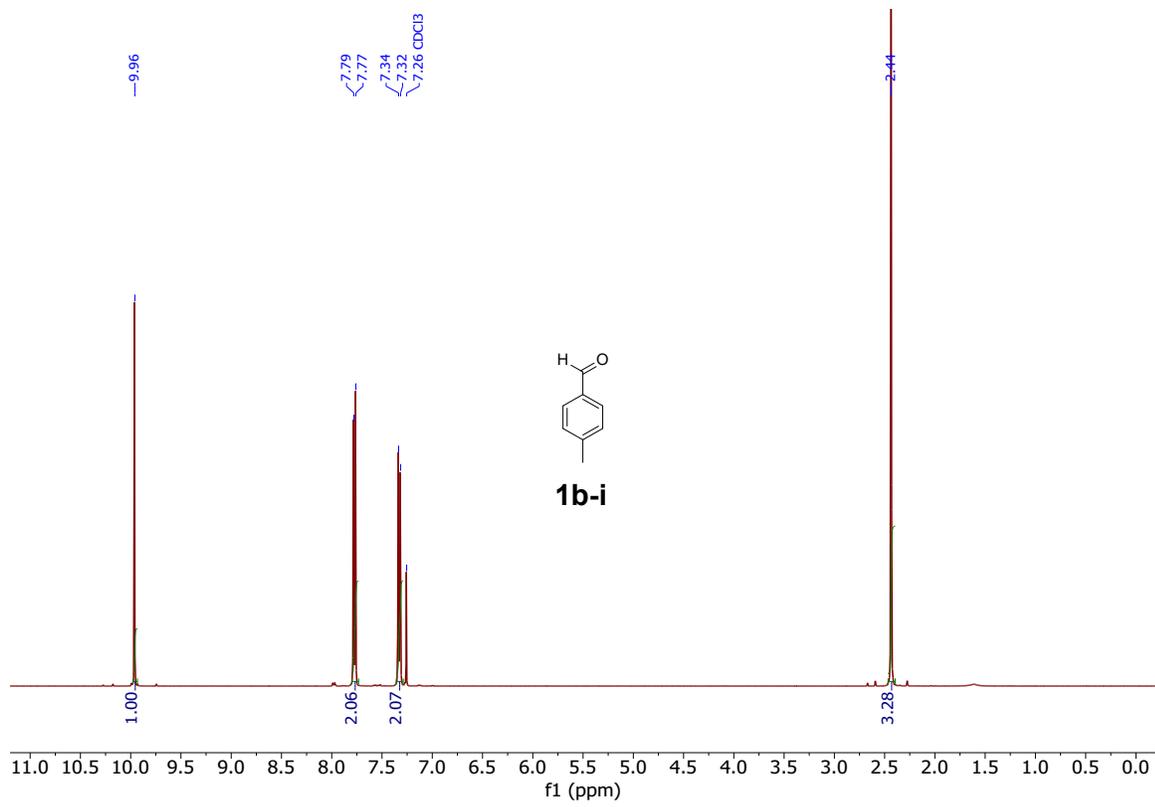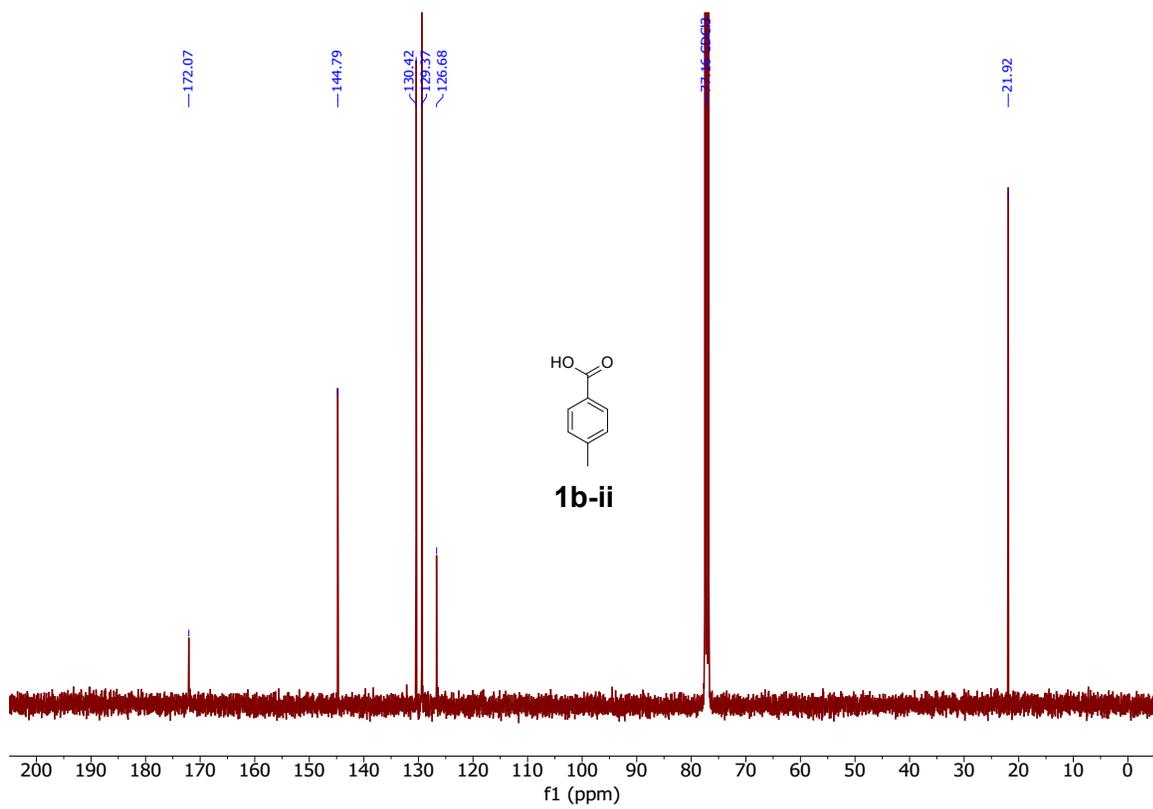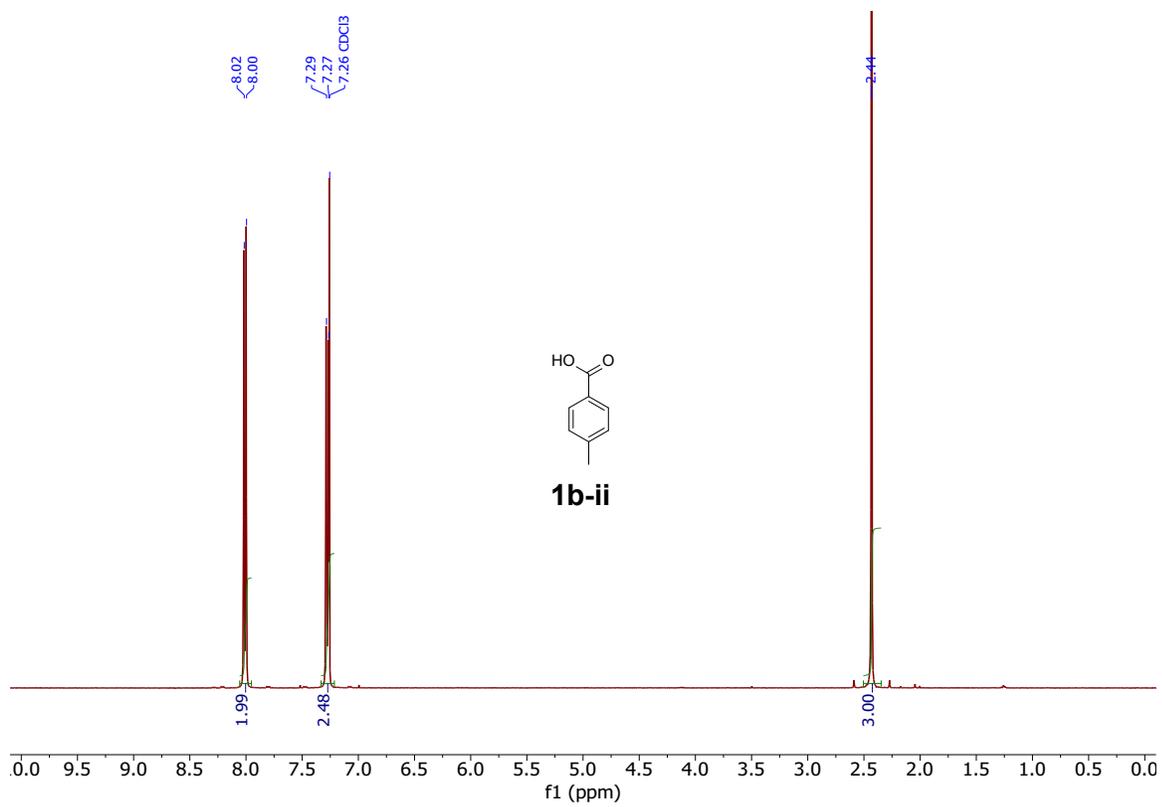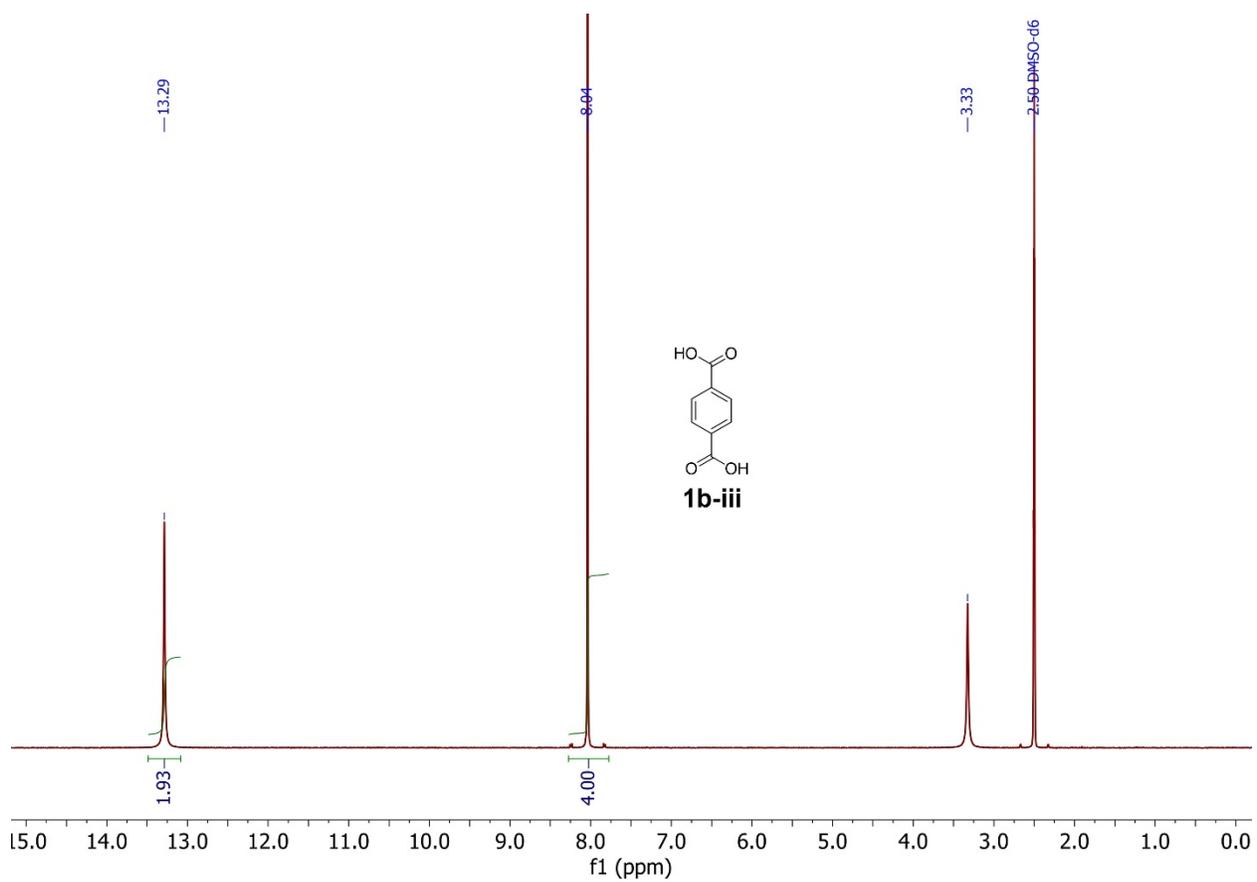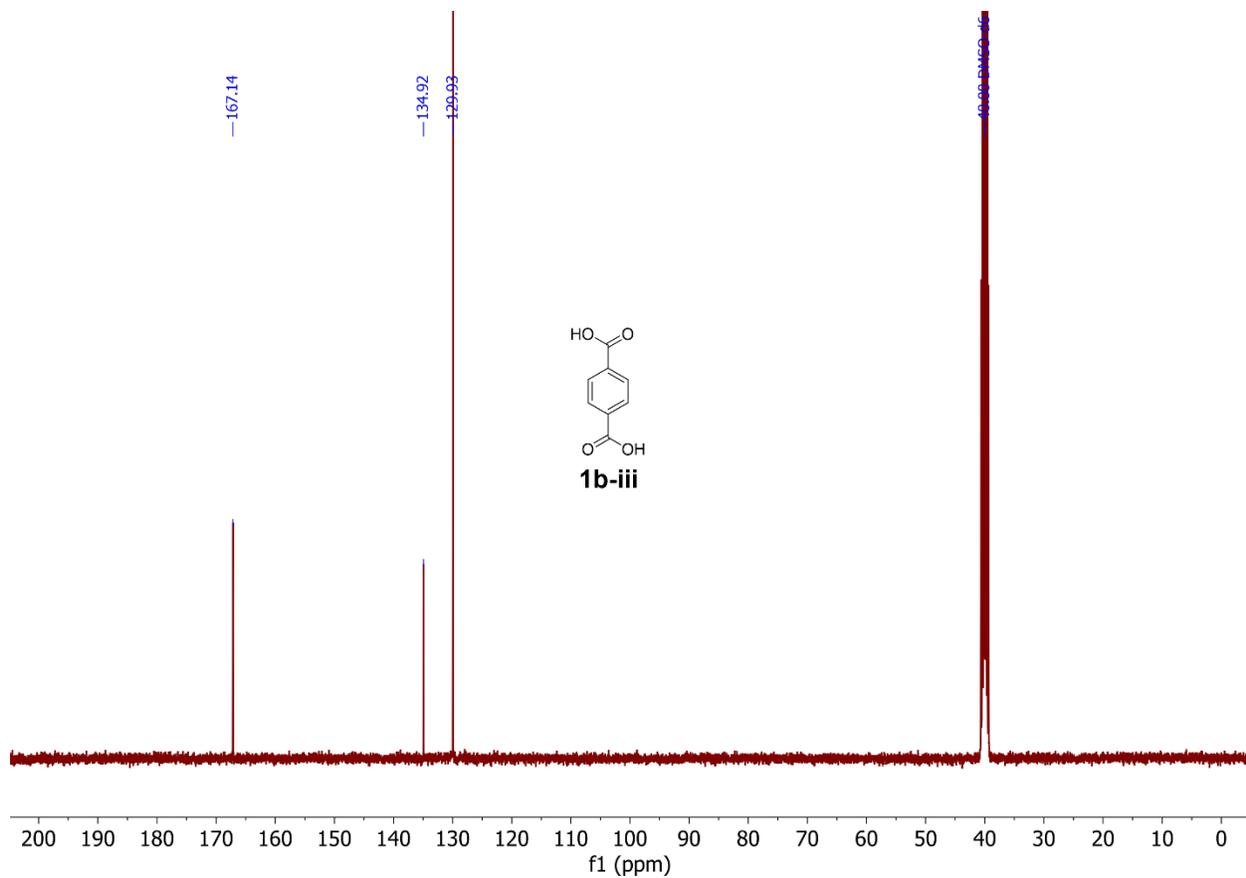14) 2-Benzofuran-1(3H)-one (**1h-i**). The crude product of **1h-i** was obtained following the general procedure I-b (39 mg, 74% yield). **1h-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^1H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.55–7.49 (m, 2H), 5.32 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$): δ 171.2, 146.7, 134.1, 129.1, 125.9, 125.9, 122.2, 69.8. NMR spectral data were consistent with those available in the literature (*Adv. Synth. Catal.* **2011,** *353*, 401-410).

15) 2-Benzofuran-1,3-dione (**1h-ii**). The crude product of **1h-ii** was obtained following the general procedure I-b (11 mg based on the collection of five trials, 15% average yield). **1h-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^1H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.03 (m, 2H), 7.93 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CD$_2$Cl$_2$): δ 163.5, 136.7, 131.8, 126.2. NMR spectral data were consistent with those available in the literature (*J. Org. Chem.* **2006,** *71*, 4516-4520).
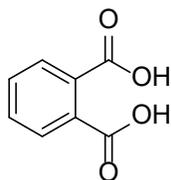
16) Phthalic acid (**1h-iii**). The crude product of **1h-iii** was obtained following the general procedure I-b (8 mg based on the collection of five trials, 10% average yield). **1h-iii** was purified by silica gel flash column chromatography (MeCN: CH$_2$Cl$_2$ = 10: 1) and isolated as a white solid. ^1H NMR (400 MHz, DMSO-d_6): δ 13.1 (br, 2H), 7.67 (m, 2H), 7.58 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 168.7, 132.8, 130.8, 128.3. NMR spectral data were consistent with those available in the literature (*Bull. Chem. Soc. Jpn.* **2004,** *77*, 1745-1755).

17) 3,4-Dihydro-1H-2-benzopyran-1-one (**1i-i**). The crude product of **1i-i** was obtained following the general procedure I-b (8 mg, 52% average yield). **1i-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 4.52 (t, J = 6.0 Hz, 2H), 3.04 (t, J = 6.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 165.2, 139.6, 133.7, 130.3, 127.7, 127.3, 125.3, 67.4, 27.8. NMR spectral data were consistent with those available in the literature (*Adv. Synth. Catal.* **2011,** *353,* 401-410).
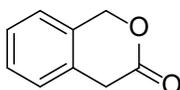
18) 1,4-Dihydro-3H-isochromen-3-one (**1i-ii**). The crude product of **1i-ii** was obtained following the general procedure I-b (9 mg based on the collection of five trials, 12% average yield). **1i-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (m, 2H), 7.24 (m, 2H), 5.32 (s, 2H), 3.72 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 170.8, 131.7, 131.1, 129.0, 127.5, 127.3, 124.8, 70.3, 36.4. NMR spectral data were consistent with those available in the literature (*J. Org. Chem.* **2004,** *69*, 7552-7557).

19) 2-Thiophenecarbaldehyde (**1j-i**). The crude product of **1j-i** was obtained following the general procedure II-b (13 mg based on the collection of three trials, 39% average yield). **1j-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.92 (s, 1H), 7.77–7.73 (m, 2H), 7.20–7.18 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 183.1, 144.1, 136.4, 135.2, 128.4. NMR spectral data were consistent with those available in the literature (*Org. Lett.* **2004,** *6,* 4821-4824).
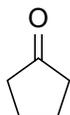
20) Cyclopentanone (**1k-ii**). The crude product of **1k-ii** was obtained following the general procedure II-b (15 mg based on the collection of two trials, 86% average yield). **1k-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.15–2.12 (m, 4H), 1.95–1.91 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 220.8, 38.4, 23.3. NMR spectral data were consistent with those available in the literature (*J. Am. Chem. Soc.* **2016,** *138,* 10128-10131).
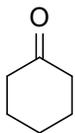
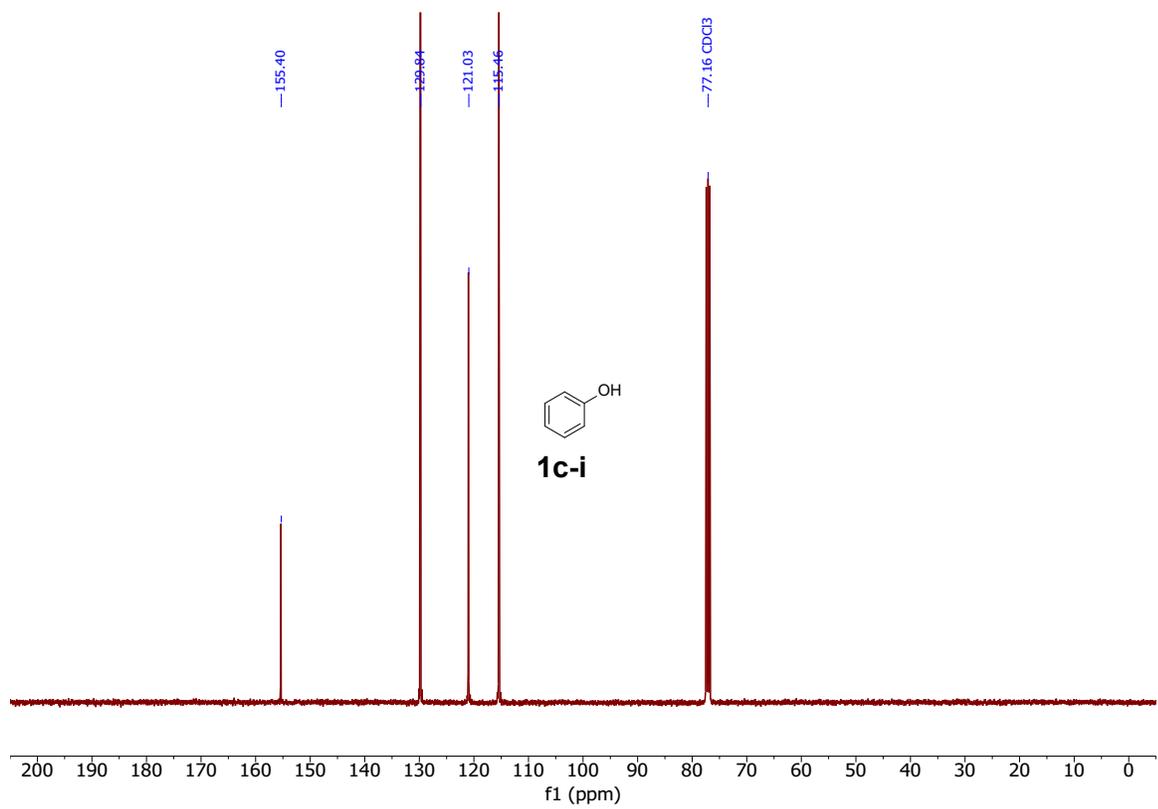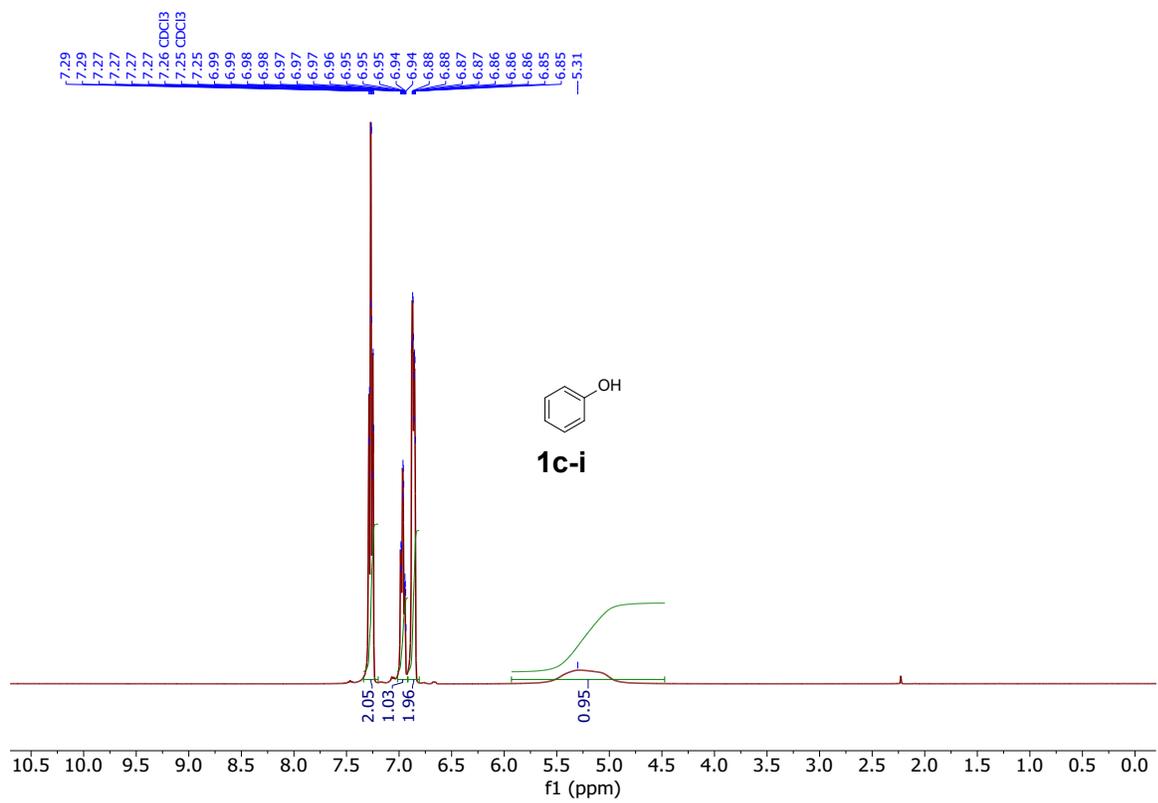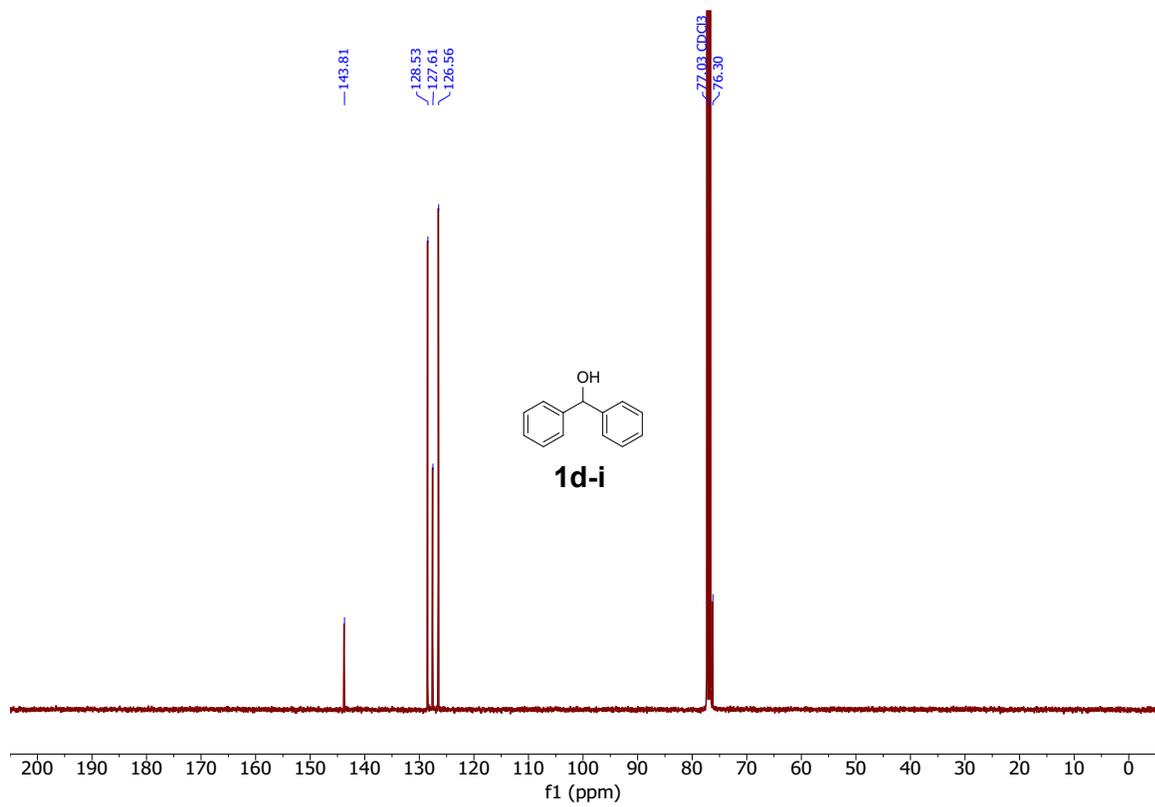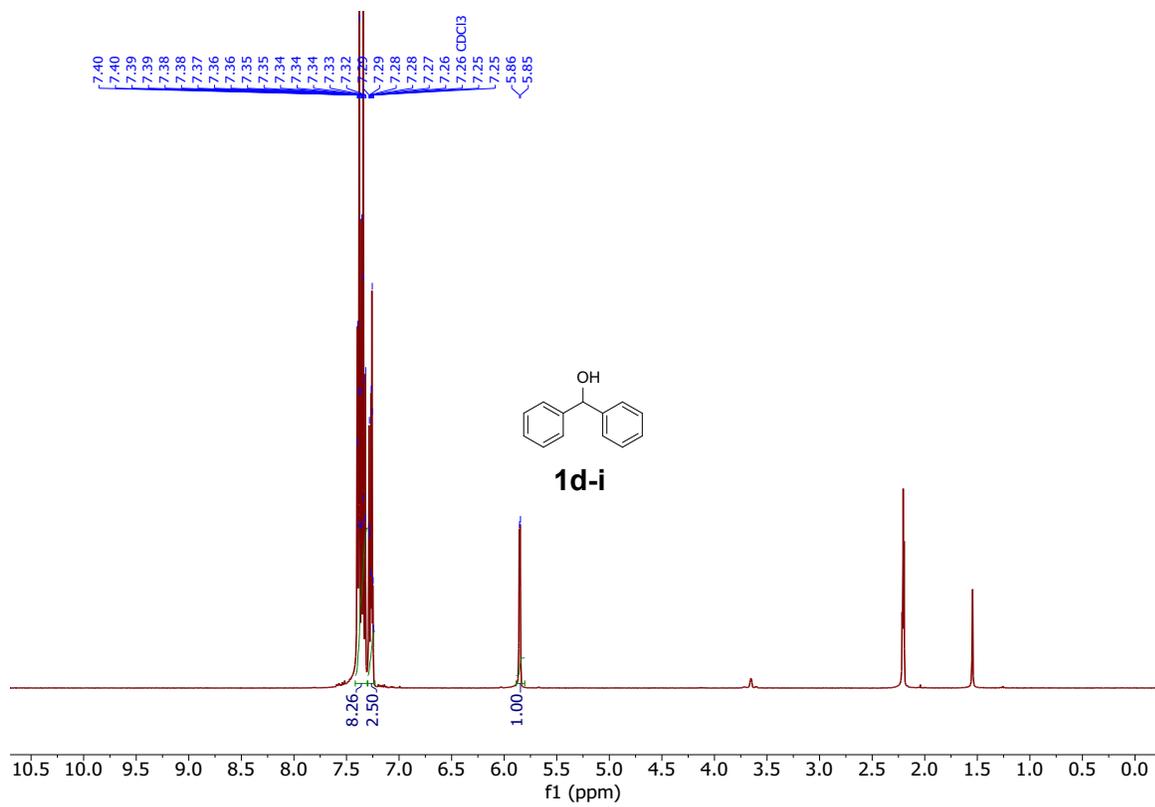21) Cyclohexanone (**1l-ii**). The crude product of **1l-ii** was obtained following the general procedure II-b (13 mg based on the collection of three trials, 43% average yield). **1l-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.32–2.27 (m, 4H), 1.86–1.79 (m, 4H), 1.70–1.68 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 212.2, 42.1, 27.1, 25.1. NMR spectral data were consistent with those available in the literature (*J. Am. Chem. Soc.* **2016,** *138,* 10128-10131).

22) Cyclooctanol (**1m-i**). The crude product of **1m-i** was obtained following the general procedure I-b (15 mg, 30% average yield). **1m-i** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.81 (m, 1H), 1.83–1.76 (m, 2H), 1.69–1.62 (m, 4H), 1.60–1.44 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 72.2, 34.8, 27.5, 25.3, 22.8. NMR spectral data were consistent with those available in the literature (*J. Am. Chem. Soc.* **2016,** *138,* 10128-10131).
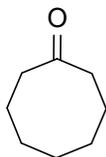
23) Cyclooctanone (**1m-ii**). The crude product of **1m-ii** was obtained following the general procedure I-b (22 mg, 44% yield). **1m-ii** was purified by silica gel flash column chromatography (hexane: EtOAc = 20: 1) and isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.41–2.38 (m, 4H), 1.89–1.83 (m, 4H), 1.56–1.51 (m, 4H), 1.39–1.33 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 218.4, 42.1, 27.3, 25.8, 24.8. NMR spectral data were consistent with those available in the literature (*J. Am. Chem. Soc.* **2016,** *138,* 10128-10131).

1a-ii

1a-ii

1a-iii

1a-iii

1b-i

1b-i

1b-ii

1b-ii

1b-iii

167.14

134.92
129.93

40.00 DMSO-d6

HO
O
O
OH

1b-iii

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1c-i

1c-i

1d-i

1d-i

1d-ii

1d-ii

1e-i

1e-i

1f-i

1f-i

1f-ii

1f-ii

1g-i

1g-i

1g-ii

1g-ii

1h-i

1h-i

1h-ii

1h-ii

1h-iii

1h-iii

1i-i

1i-i

1i-ii

1i-ii

1j-i

9.92
9.91
7.77
7.77
7.77
7.76
7.76
7.75
7.75
7.74
7.74
7.74
7.73
7.26 CDCl3
7.20
7.19
7.19
7.18

1.00

2.01

0.95

f1 (ppm)

1j-i

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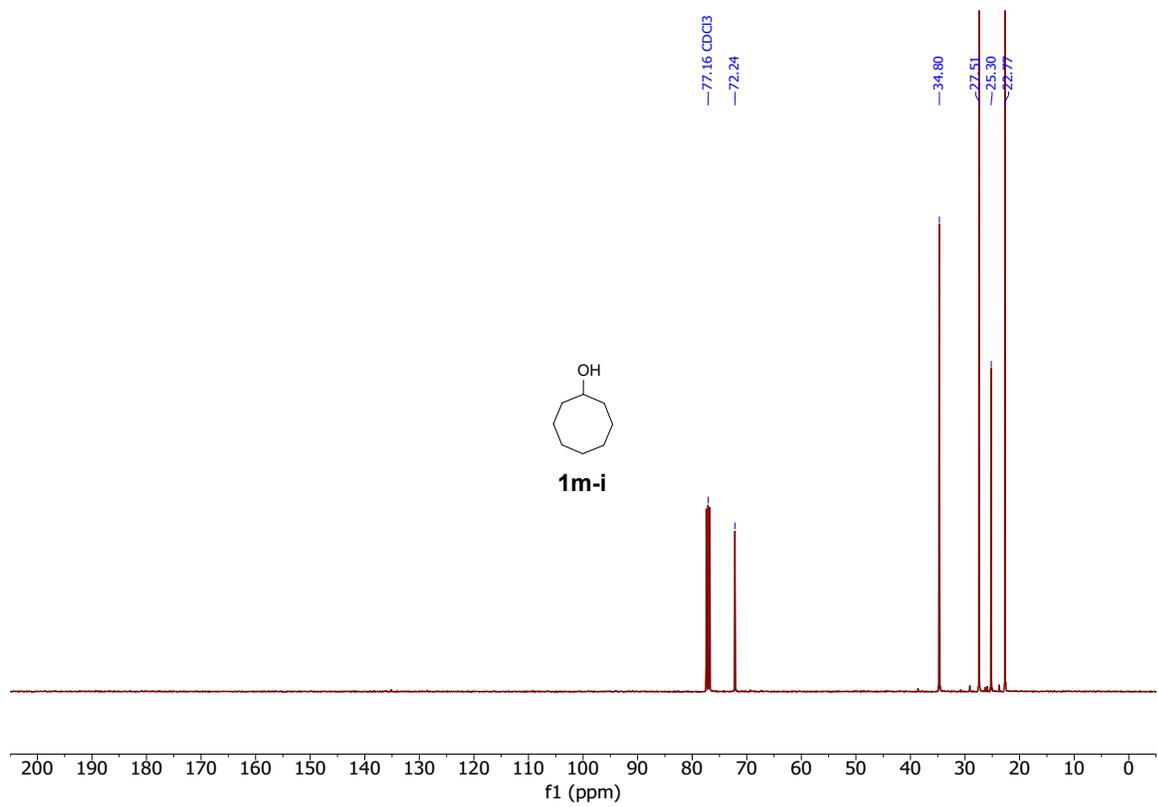
f1 (ppm)

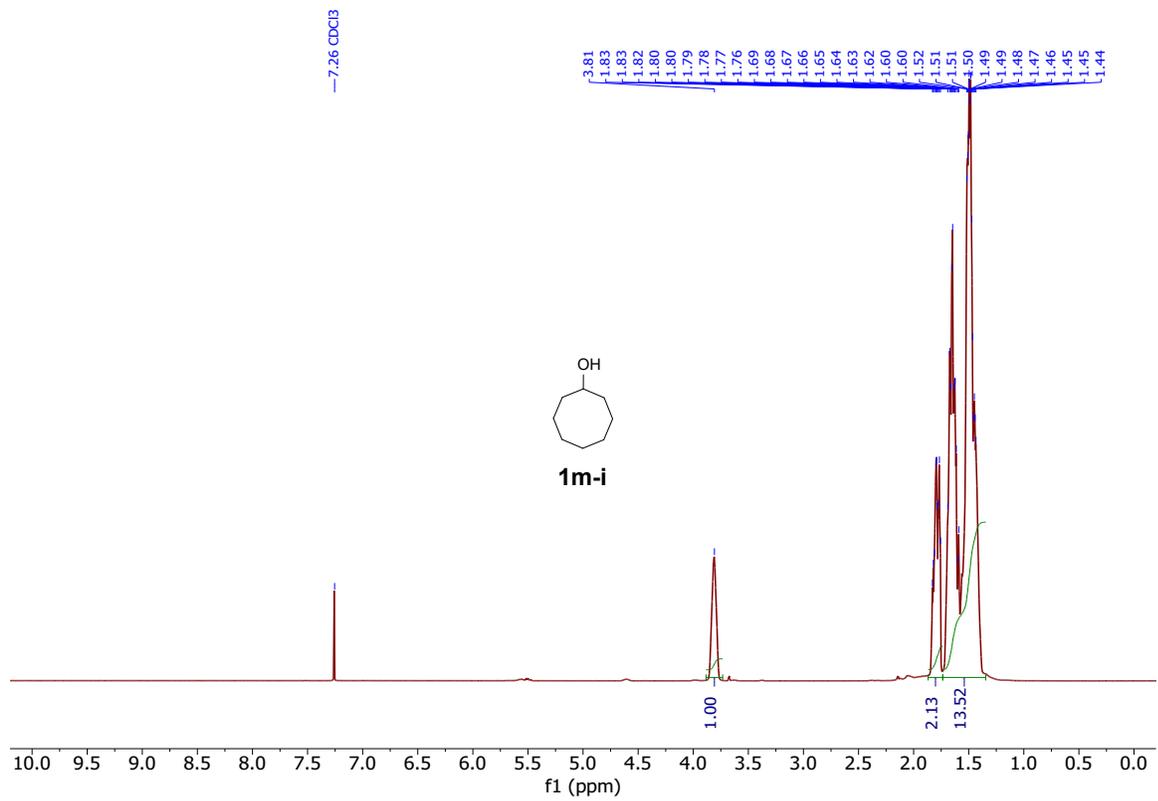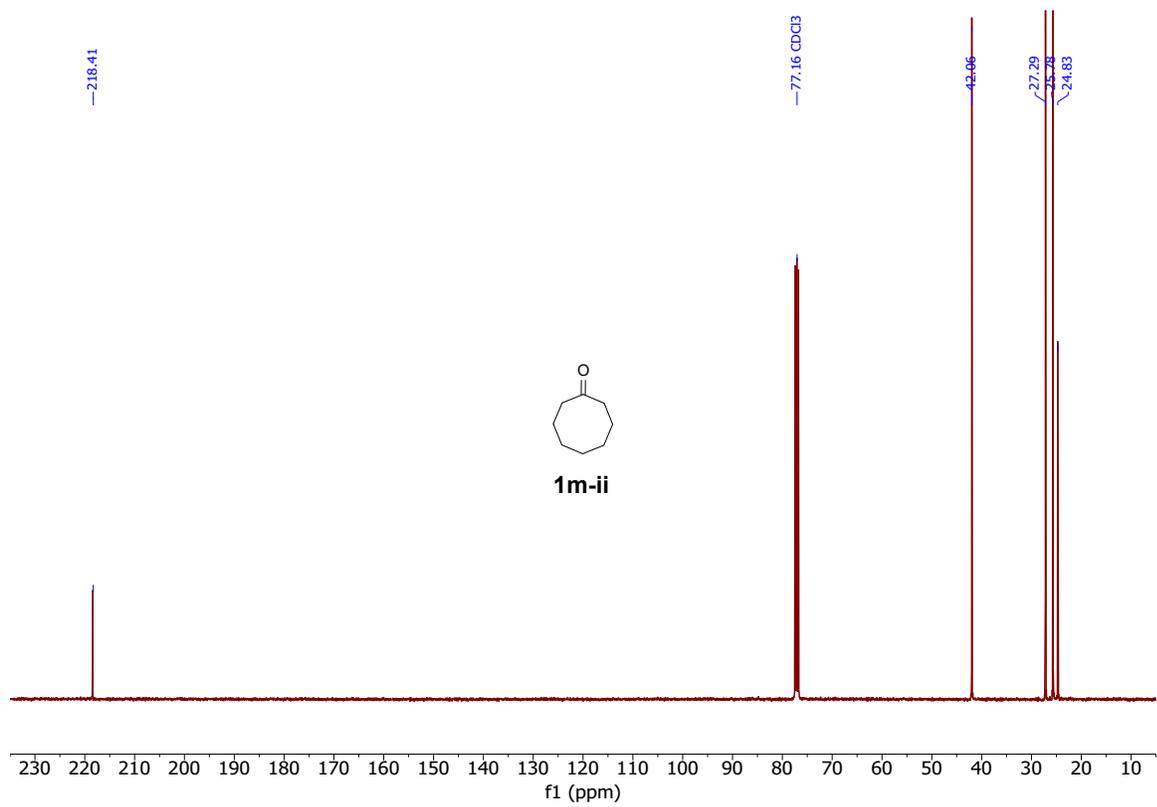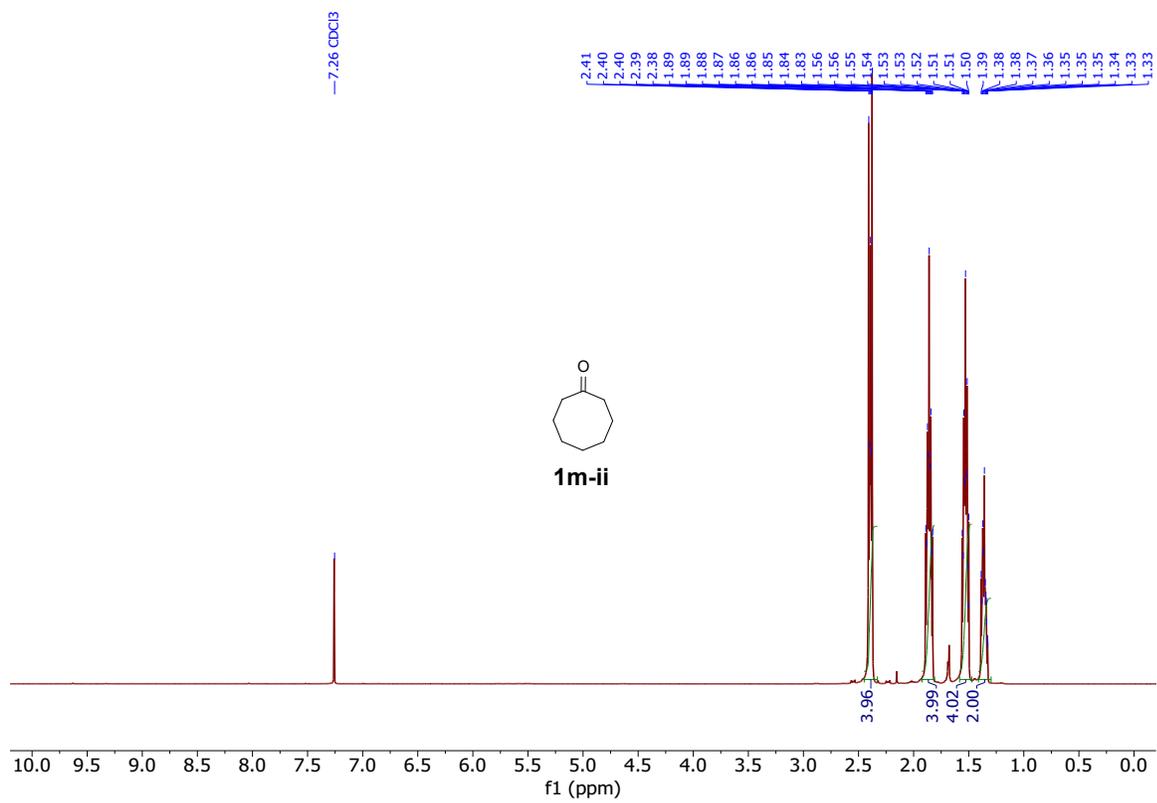1k-ii

1k-ii

1l-ii

1l-ii

1m-ii
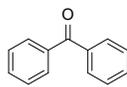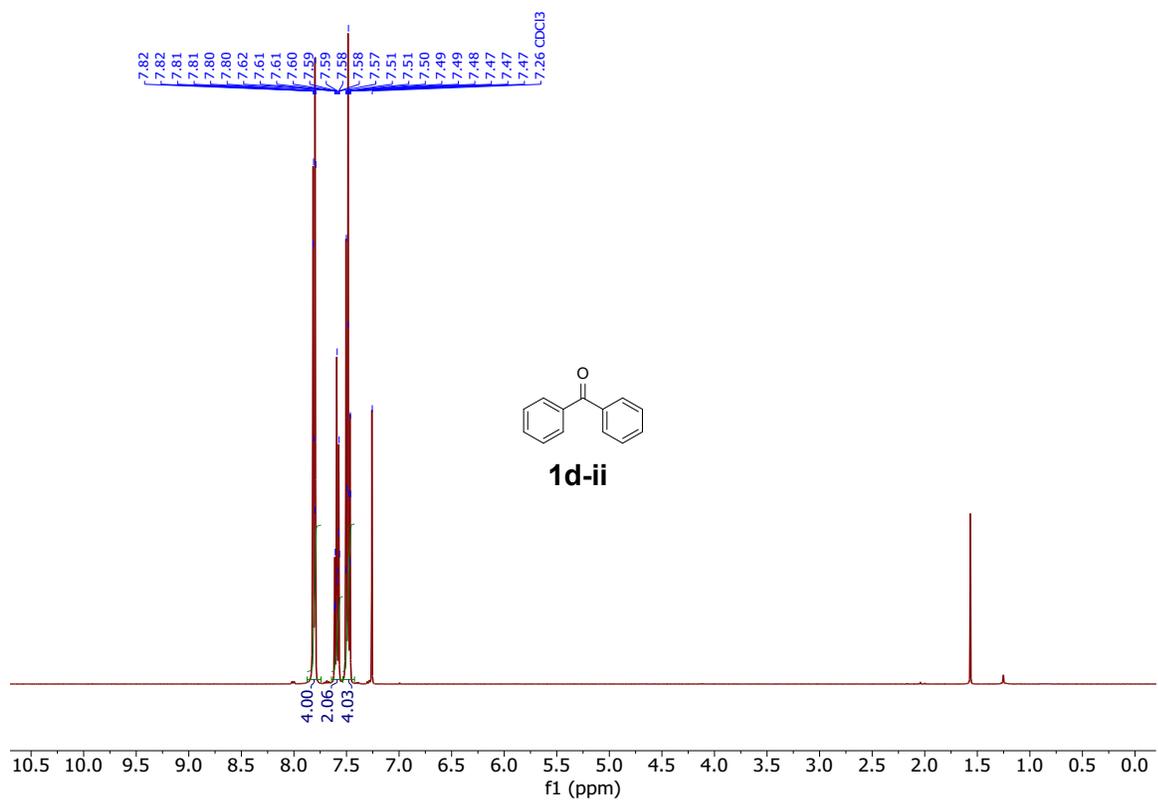
1m-ii

XIV. References

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