Supporting Information

Water enhanced photo-oxidation of alcohols on colloidal quantum dots

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General Information

Chemicals and reagents

Cadmium chloride (CdCl$_2$, 99.8%, Merck), Sodium sulfide (Na$_2$S, 99.8%, Macklin), 3-Mercaptopropionic acid (MPA, 85%, TCI), Sodium hydroxide (NaOH, Aladdin), Benzyl alcohol (BA, 80-90%, Macklin), Benzaldehyde (BAD, 99.9%, Macklin), Acetonitrile (AR, >99%, Aladdin) were used as purchased without any further purification. Ultrapure water (18.2 MΩ) was used in all experiments.

Apparatus and measurements

The crystal structures of QDs were measured using a Bruker D8 advance with Cu Kα radiation at 40 kV and 30 mA, the X-ray diffraction (XRD) scans were taken from 5° to 90° with a scan rate of 2°/min. The UV-vis spectra were recorded on a Specord 2010 Plus (analytikjena) UV-vis absorption spectrometer with a resolution of 1 nm and a scan rate of 20 nm/s. For transmission electron microscope (TEM) measurements, the purified QDs precipitates were obtained by drying a drop of diluted QDs suspension on the surface of a 200-mesh copper TEM grid under ambient condition. The samples were characterized using a Talos F200X G2 electron microscope (AEMC) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) and ultroviolet photoelectron spectroscopy (UPS) were performed on a Thermo Fisher Scientific EscaLab 250Xi using an Al Kα radiation source. Steady-state photoluminescence (PL) spectra were collected on a molecular fluorescence spectrometer (F-4600) under excitation at 420 nm with a scan step of 1 nm. Electron paramagnetic resonance (EPR) was employed to characterize active species in the benzyl alcohol oxidation reaction. EPR spectra were recorded on a Bruker A300-10/12 ESR spectrometer with an Xe lamp (300 W, 400-800 nm). In a typical experiment, 8 mg of CdS QDs were dispersed in ultrapure water with 0.2 mmol benzyl alcohol. DMPO/TEMPO was used as sacrificial agent of active species during the reaction. The oxygen concentration in the reaction system was adjusted by bubbling nitrogen or oxygen into it. Fourier-transform infrared (FTIR) spectra of BA and BAD adsorption were collected using a Bruker infrared spectrometer equipped with a BaF$_2$ window, installed with inlet and outlet flows. The 60 mg QDs catalysts were placed in the sample cell and pre-treated for 2 h in an Ar gas atmosphere at 200℃. After the system was cooled down to 50℃, BA

or BAD was flowed into the sample cell for 30 min. Afterwards, the physically adsorbed molecules on QDs surface were removed by flowing Ar gas for 30 min. Finally, the FTIR spectra were collected. ^{1}H NMR spectra were measured on a Bruker AVANCE AV 400 MHz spectrometer.

Experimental Section

Note 1. Synthesis of CdS QDs

CdS QDs were synthesized according to the literature with some modifications[1]. For Cd precursor, 0.05 M of cadmium chloride ($CdCl_2$) was dispersed in a three-neck round bottom flask containing 20 mL of purified water. The mixture was initially stirred at ambient temperature. Then, 150 μL of 3-mercaptopropionic acid (3-MPA) was quickly added to it. After 5 minutes interval, the pH value of the solution was adjusted to 11 under vigorous stirring with 5 M sodium hydroxide solution. After purging with nitrogen for 30 minutes, 3 mL of sodium sulfide (Na_2S) solution (0.144 M) in the syringe was injected gently into the reaction solution under nitrogen flow. Then, the temperature of the reaction solution was increased up to 100°C for the growth of CdS nanocrystals and held for 1 hour. After the reaction, the system was cooled down to room temperature. The obtained CdS QDs were purified with water/isopropanol and precipitated via centrifugation. To obtain purified CdS QDs, the above washing process was repeated several times. Finally, the purified CdS QDs were dried in a vacuum oven and dispersed in water at a concentration of 20 mg mL^{-1}.

Note 2. Photocatalytic activity measurements

The photocatalytic reaction was performed in a 20 mL quartz tube with a magnetic stirrer. Compared to a glass tube, higher reactivity is observed using a quartz tube as the reaction vessel due to its superior light transmittance (Fig. S3†). Typically, 8 mg CdS QDs were dispersed in a quartz tube containing 0.2 mmol benzyl alcohol and 4 mL reaction solvent (water or acetonitrile). The reaction temperature was kept constant by circulating cooling water. Prior to irradiation, the suspension was stirred in the dark for 30 minutes to reach adsorption-desorption equilibrium between photocatalysts and benzyl alcohol. The

reaction system was irradiated with a 300 W Xe lamp (PLS-SEX300C, Beijing Perfectlight Technology, powder intensity ~150 mW/cm^2) for a certain time. During the reaction, 0.2 mL of aliquot was collected, extracted and centrifuged to separate reactants/products and photocatalysts at different irradiation time points. The conversion and selectivity of reaction were evaluated by gas chromatography (GC FULI 9790 II). The conversion of alcohol and aldehyde for selectivity were calculated using the following equations:

Conversion (%) = $[(C_0-C_{alcohol})/C_0] \times 100$

Selectivity (%) = $[C_{aldehyde}/(C_0-C_{alcohol})] \times 100$

Here, C_0 is the initial concentration of alcohol. $C_{alcohol}$ and $C_{aldehyde}$ is residual concentration of alcohol and the corresponding aldehyde at different time points after catalytic reaction, respectively.

In cyclic stability test, the QDs catalysts were purified with water/isopropanol and precipitated via centrifugation.

The H_2O_2 generation was qualified by using a colorimetric method from literature[2]. Typically, the reaction mixture was centrifuged and then 500 μL of the suspension was mixed with 2 mL water then extracted with 4 mL ethyl acetate. 500 μL of the water phase solution was added to a mixture of 2 mL KI solution (0.1 M) and 0.05 mL $(NH_4)_2MoO_4$ solution (0.01 M). As a positive control, a H_2O_2 standard solution (20 μL diluted to 500 μL) was also tested. Color change was recorded and the corresponding absorption was measured on a Specord 2010 plus (analytikjena) UV-vis spectrometer.

Note 3. DFT Caculations

All the density-functional theory (DFT) computations were performed using the Cambridge Sequential Total Energy Package (CASTEP) based on the pseudopotential plane wave (PPW) method. Electron-ion interactions were described using the ultrasoft (USP) potentials. A plane-wave basis set was employed to expand the wave functions with a cutoff kinetic energy of 520 eV. For the electron-electron exchange and

correlation interactions, the functional parametrized by Perdew-Burke-Ernzerhof (PBE), a form of the general gradient approximation (GGA), was used throughout.

During the geometry optimizations, all the atom position were allowed to relax. In this work, the Brillouin-zone integrations were conducted using Monkhorst-Pack (MP) grids of special points with the separation of 0.06 Å-1. The convergence criterion for the electronic self-consistent field (SCF) loop was set to 2×10-6 eV/atom. The atomic structures were optimized until the residual forces were below 0.05 eVÅ-1. The vander Waals interaction was described using the DFT-D2 method that proposed by Grimme. All adsorptive binding energies (E_{ads}) used in this paper were defined as：

$$E_{ads} = E_{total} - (E_a + E_b)$$

where the E_{total} is the total energy of the adsorbate interacting system and E_a and E_b are the energies of the slab and the isolated adsorbate, respectively.
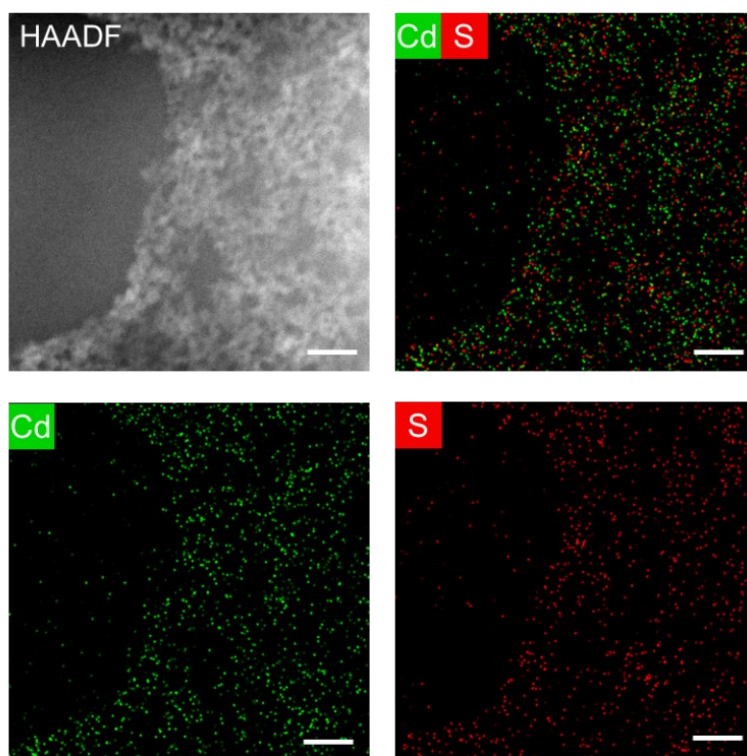
Figure S1. HAADF image of the CdS QDs and the corresponding EDS mapping results of Cd and S. Scare bares, 20 nm.
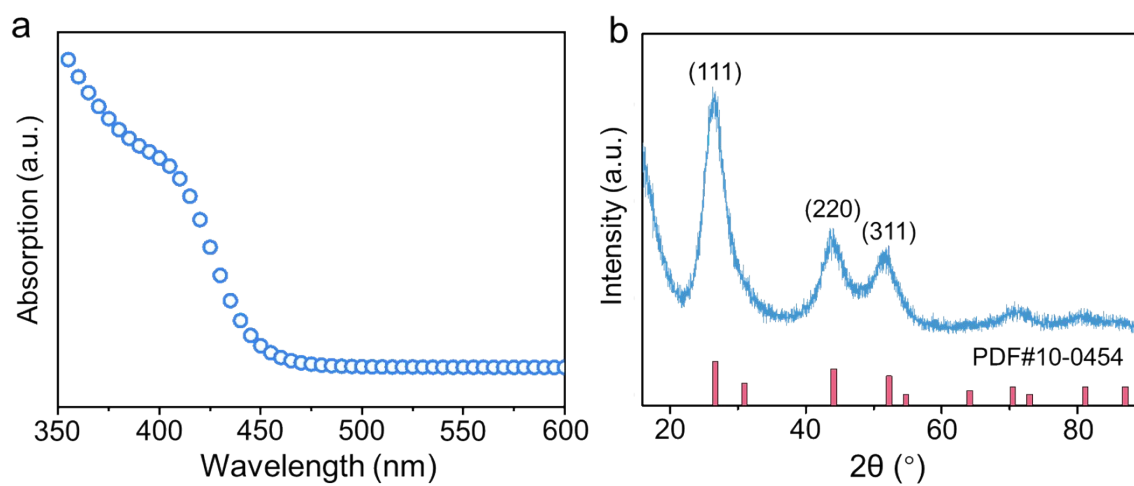
Figure S2. (a) UV-vis absorption spectra of CdS QDs. (b) XRD pattern of CdS QDs.
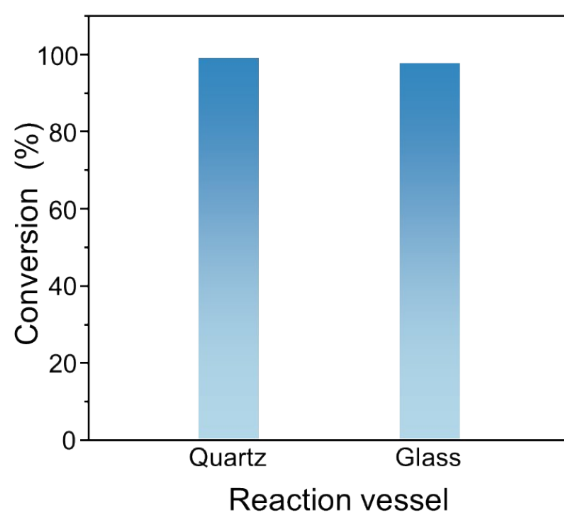
Figure S3. The comparison of photocatalytic activity using different reaction vessels.
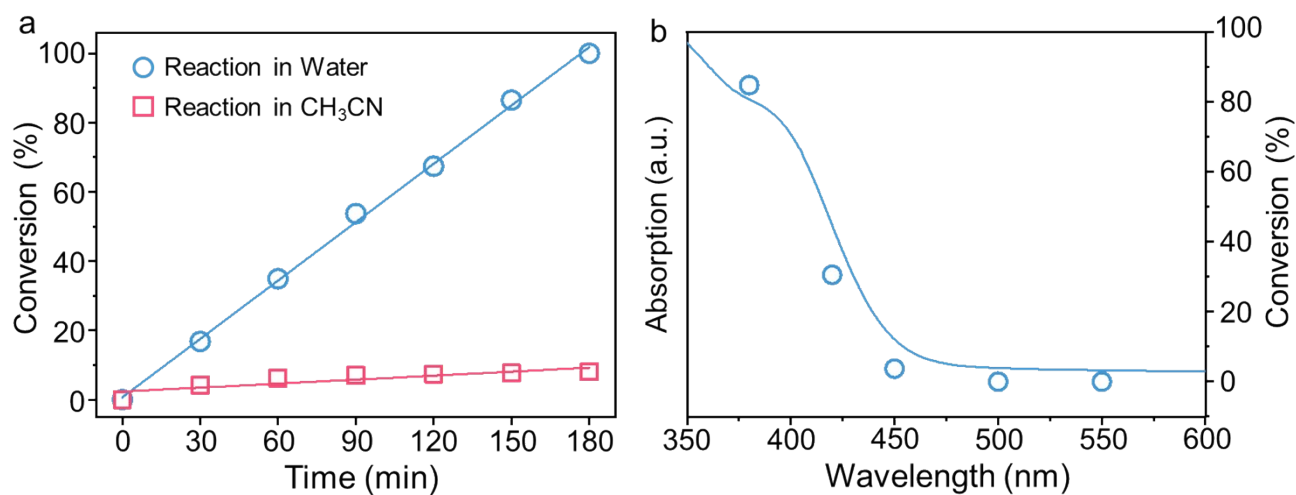
Figure S4. (a) The conversion of benzyl alcohol under visible light (400-800 nm) in pure water and pure acetonitrile, respectively (powder intensity ~180 mW/cm^2). (b) UV-vis absorption spectra of CdS QDs and photocatalytic activity of CdS QDs at 380, 420, 450, 500, 550 nm, respectively.
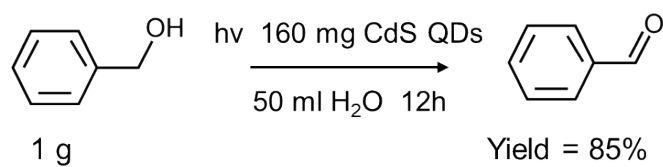
Figure S5. Scale-up synthesis of benzyl aldehyde.
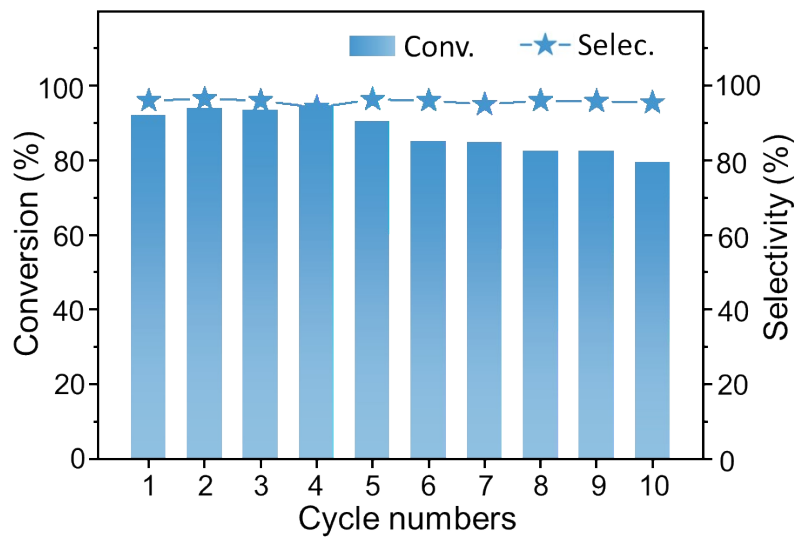
Figure S6. The photocatalytic stability of the CdS QDs for benzyl alcohol oxidation reaction.
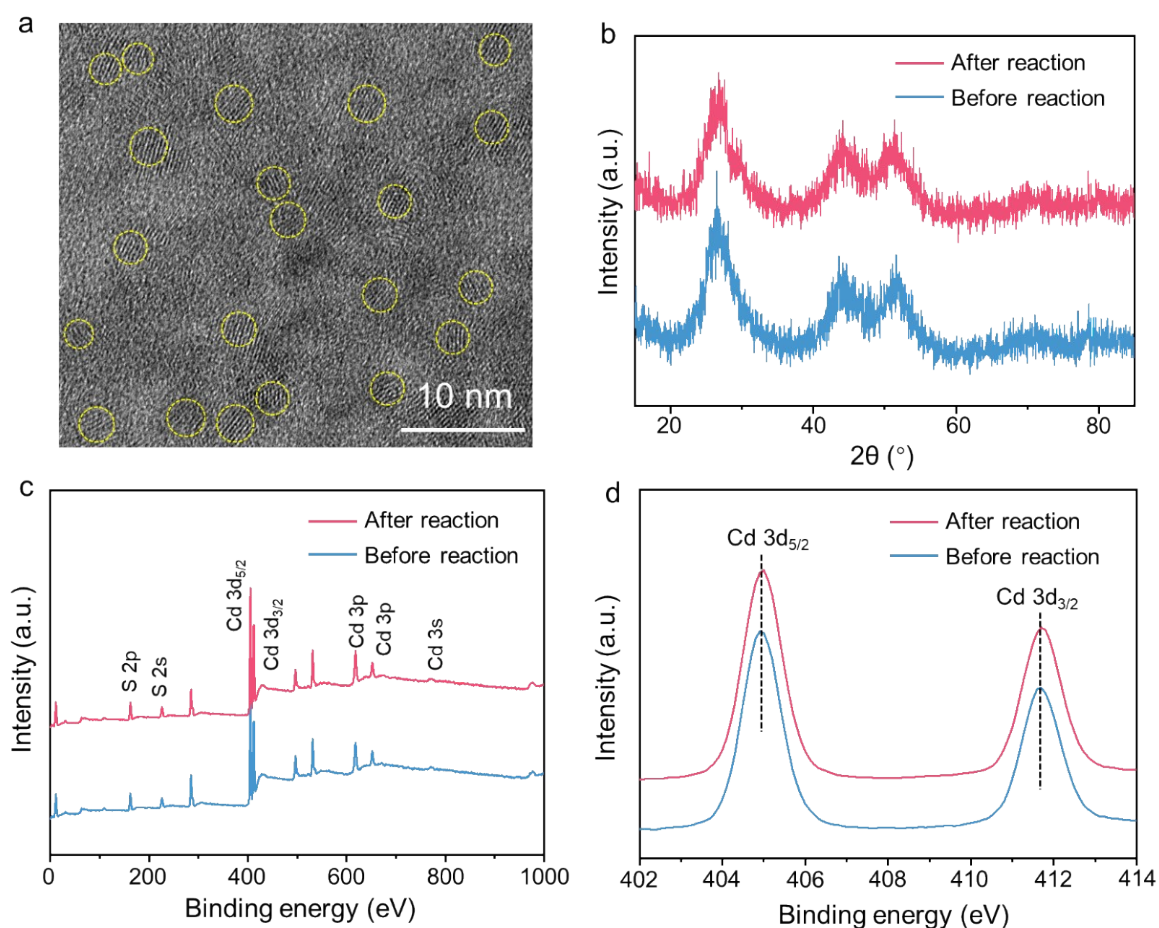
Figure S7. (a) TEM image of CdS QDs after the catalytic reaction. (b) XRD patterns of CdS QDs before and after the catalytic reaction. (c), (d) XPS analysis of CdS QDs before and after the catalytic reaction.
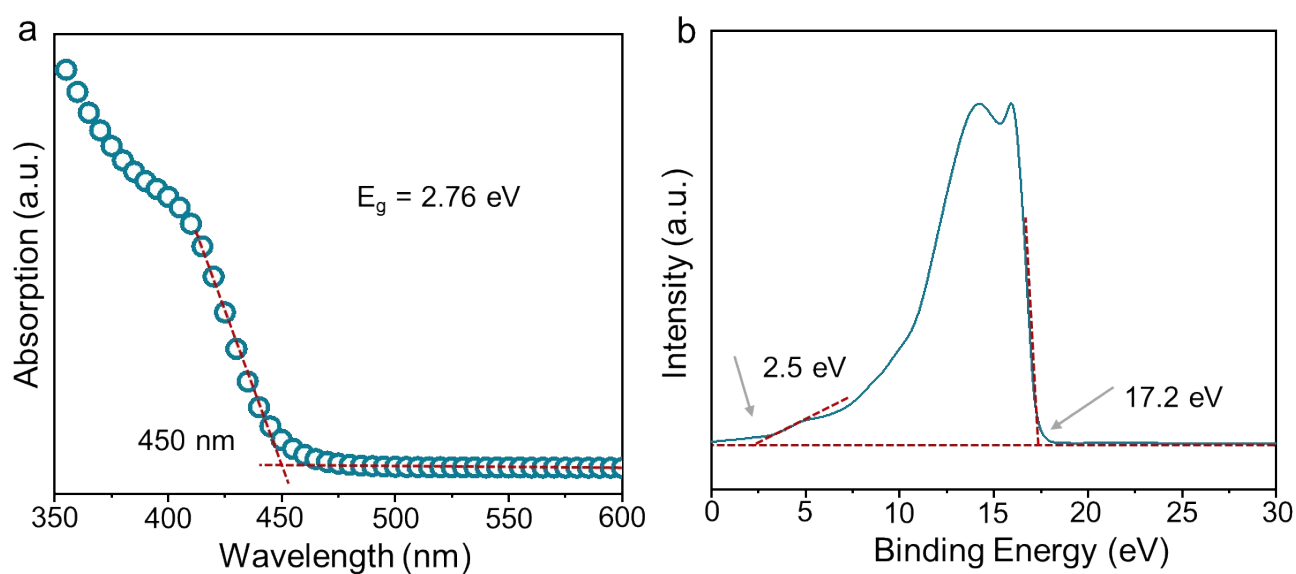
Figure S8. Valence band spectra of CdS QDs.
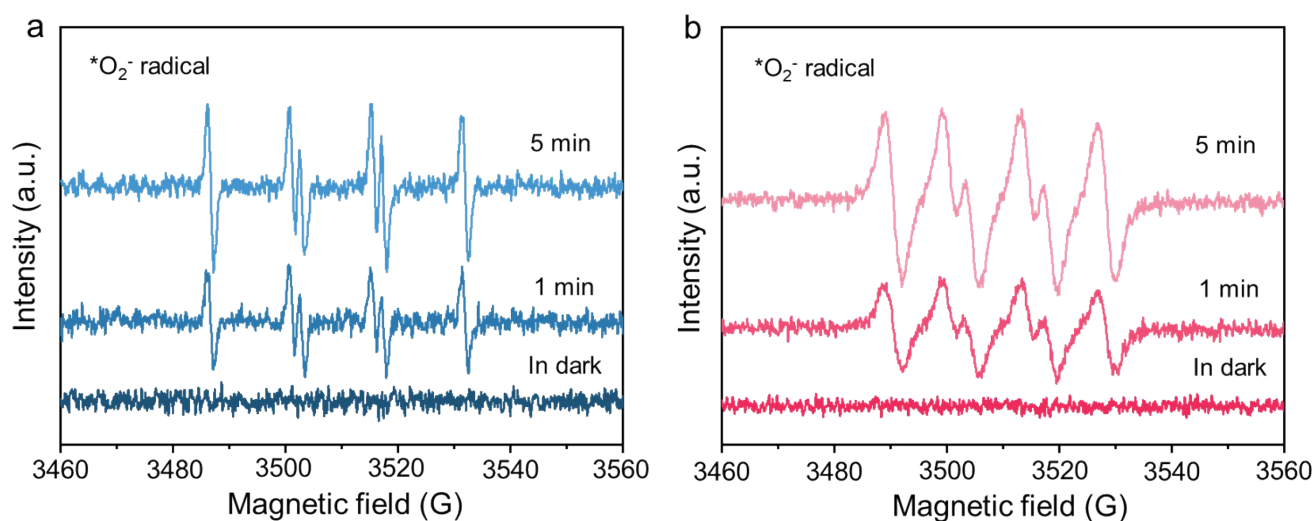
Figure S9. EPR spectra of in-situ formed superoxide radical in water medium (blue) and acetonitrile solvent (pink), respectively.
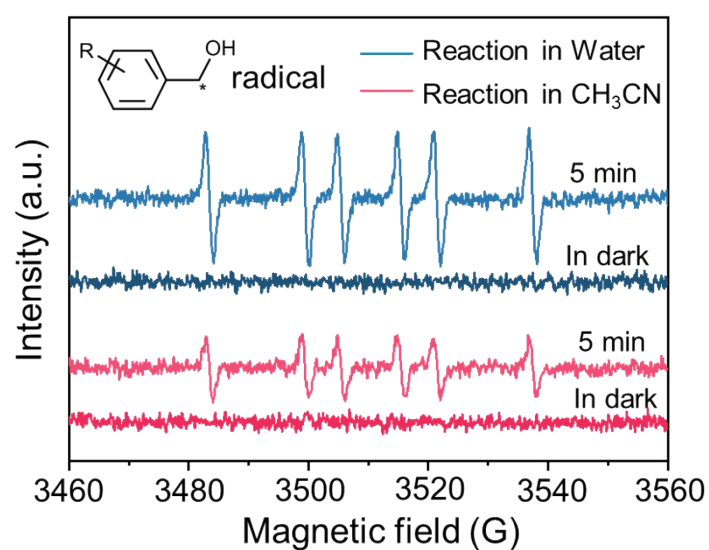
Figure S10. EPR spectra of in-situ formed carbon-centered radical in water medium (blue) and acetonitrile solvent (pink), respectively.
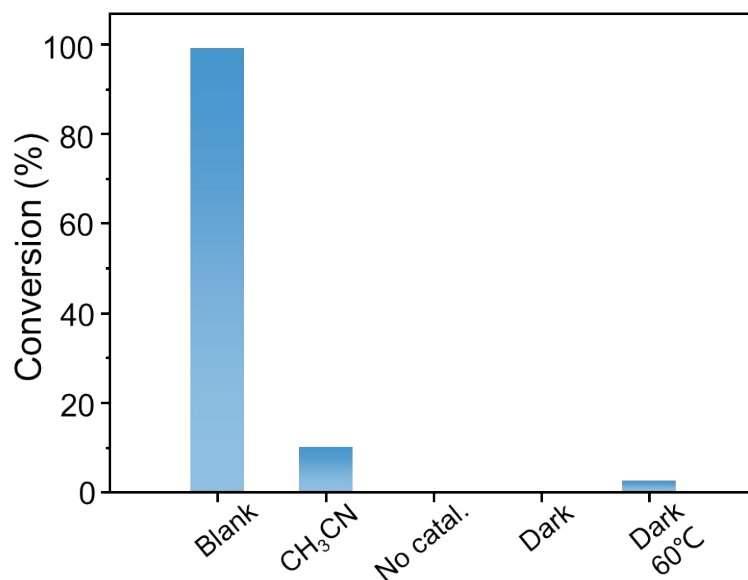
Figure S11. Control tests for benzyl alcohol oxidation reaction in water medium under different conditions.
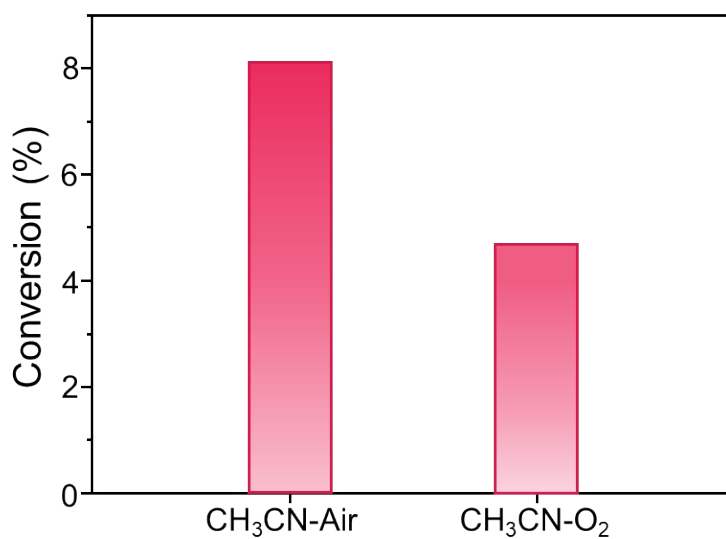
Figure S12. Photocatalytic performance of CdS QDs for benzyl alcohol oxidation in acetonitrile solvent with different oxygen concentrations.
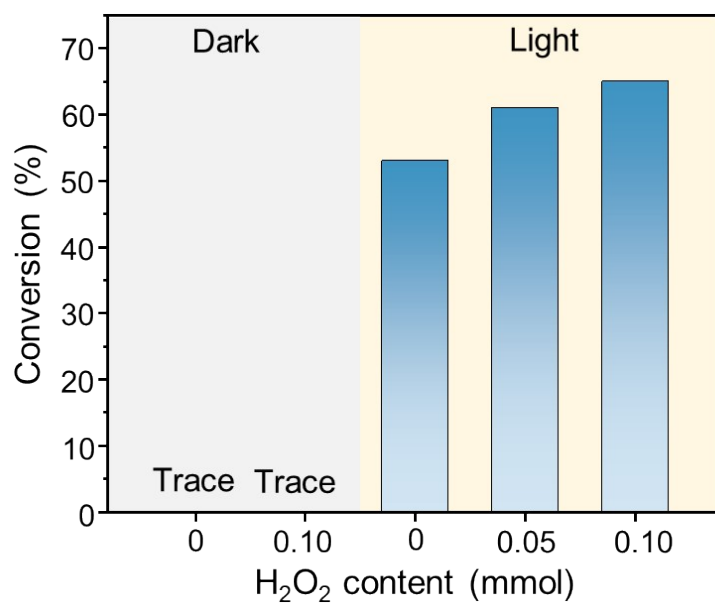
Figure S13. The effect of H_2O_2 content on photocatalytic activity.
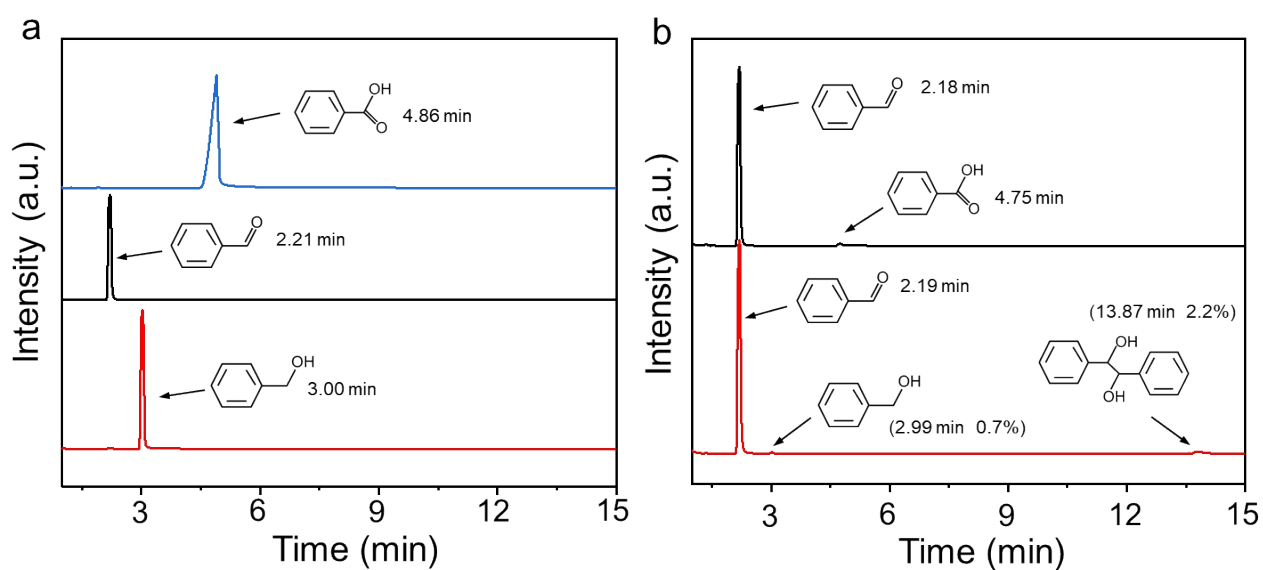
Figure S14. (a) Gas chromatography spectra of BA and BAD. (b) Gas chromatography spectra of benzoic acid produced in the reaction solution of BA (red) and BAD (black).
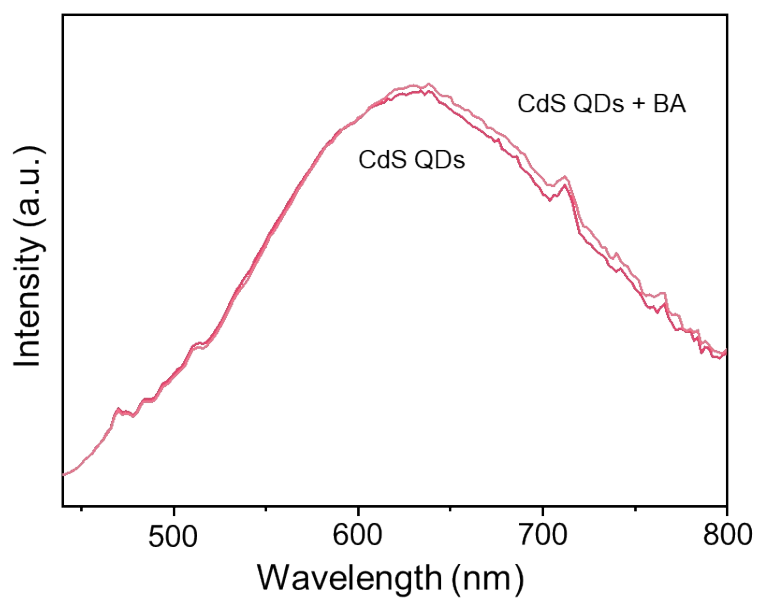
Figure S15. Photoluminescent emission of CdS QDs in acetonitrile solvent before and after adding benzyl alcohol.
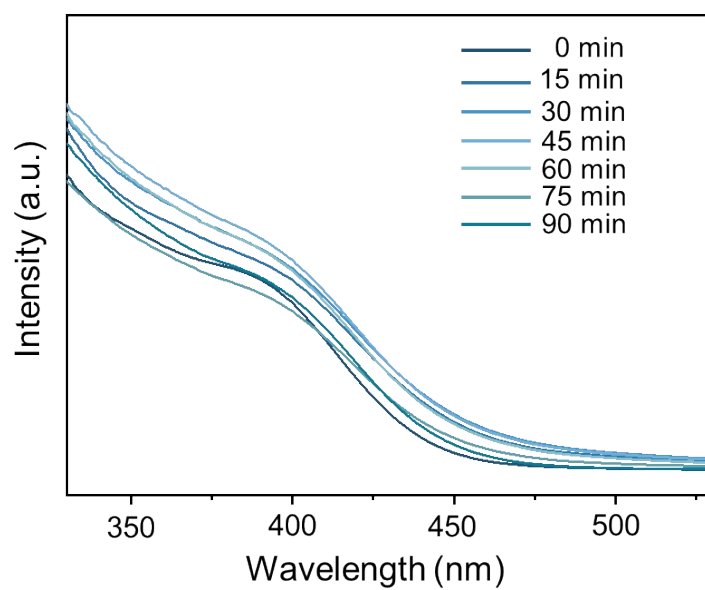
Figure S16. The absorption spectra of CdS QDs as a function of different reaction times.
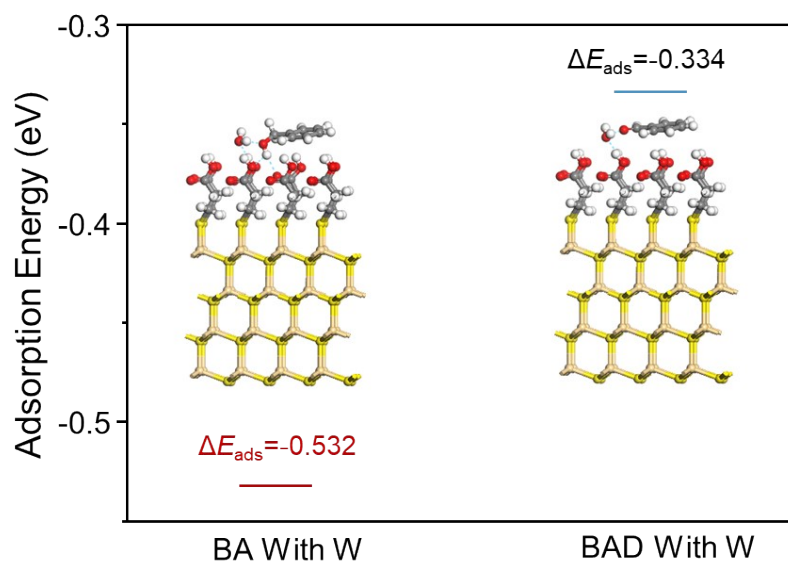
Figure S17. Adsorption energy of benzyl alcohol and benzaldehyde over CdS QDs with the presence of water.
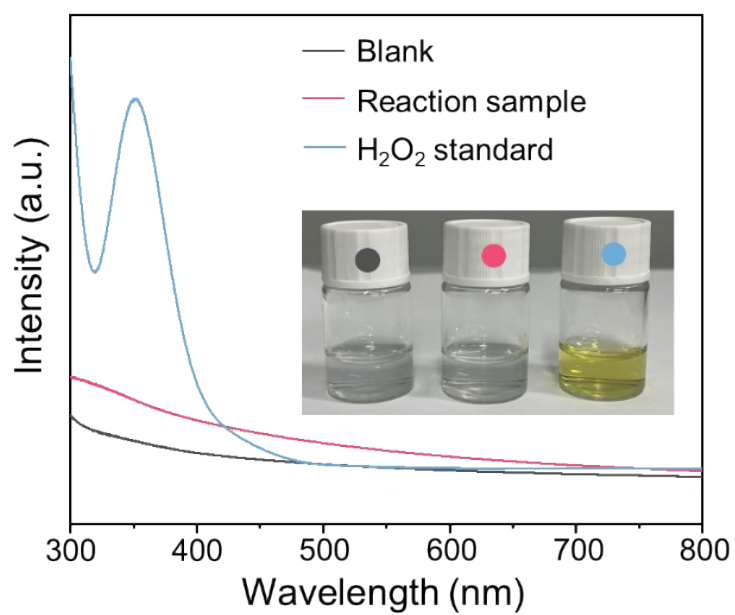
Figure S18. The qualification of the H_2O_2 generation.

References

1. Aboulaich, A.; Billaud, D.; Abyan, M.; Balan, L.; Gaumet, J.; Medjadhi, G.; Ghanbaja, J.; Schneider, R., One-Pot noninjection route to CdS quantum dots via hydrothermal synthesis. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2561-2569.

2. Zhou, L.; Feng, J. R.; Qiu, B. C.; Zhou, Y.; Lei, J. Y.; Xing, M. Y.; Wang, L. Z.; Zhou, Y. B.; Liu, Y. D.; Zhang, J. L., Ultrathin g-C_3N_4 nanosheet with hierarchical pores and desirable energy band for highly efficient H_2O_2 production. *Appl. Catal. B: Environ.* **2020**, *267*, 118396.

NMR Spectra

General Information

^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer. Chemical shifts for protons are reported in ppm and are referenced to the NMR solvent peak (CDCl$_3$: δ 7.26 ppm, DMSO-d_6: δ 2.50 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet).

[image of benzoic acid structure]
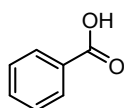
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H).

[reaction scheme: benzyl alcohol → CdS QDs, hv, 1 h → benzaldehyde]
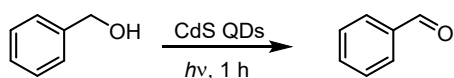
^{1}H NMR (400 MHz, CDCl$_3$) δ 10.03 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.1 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H).

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)
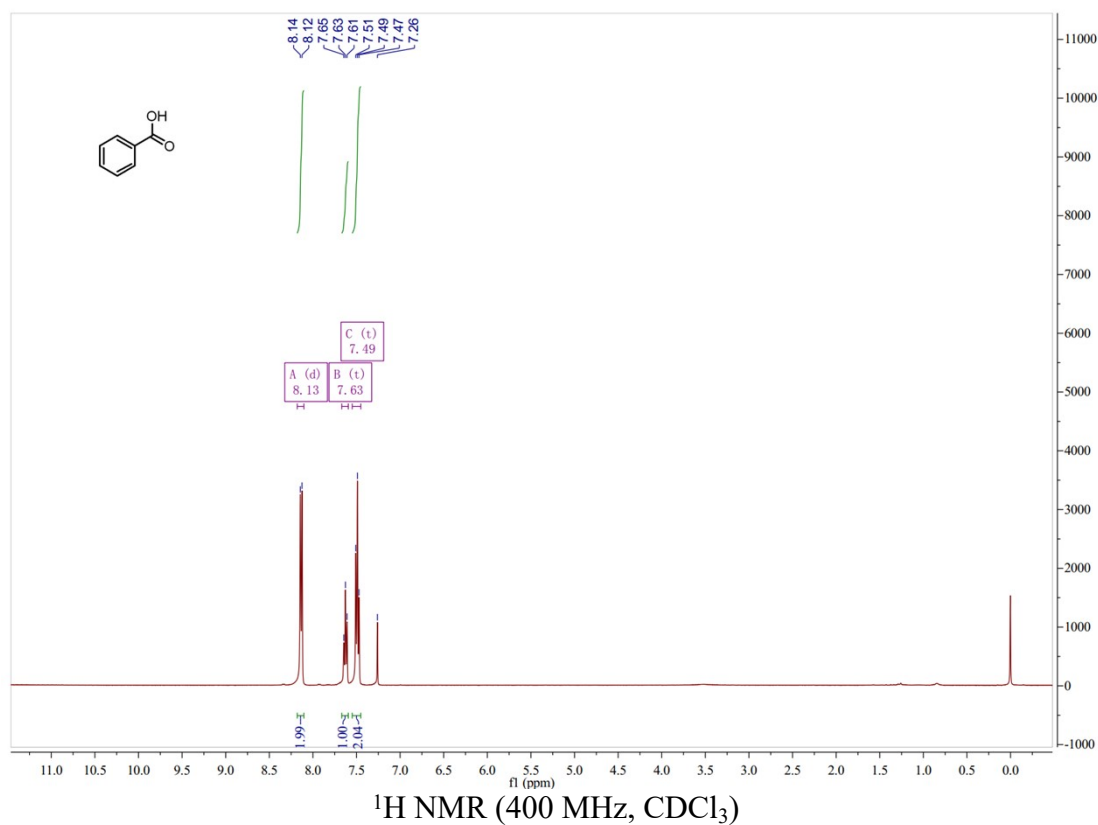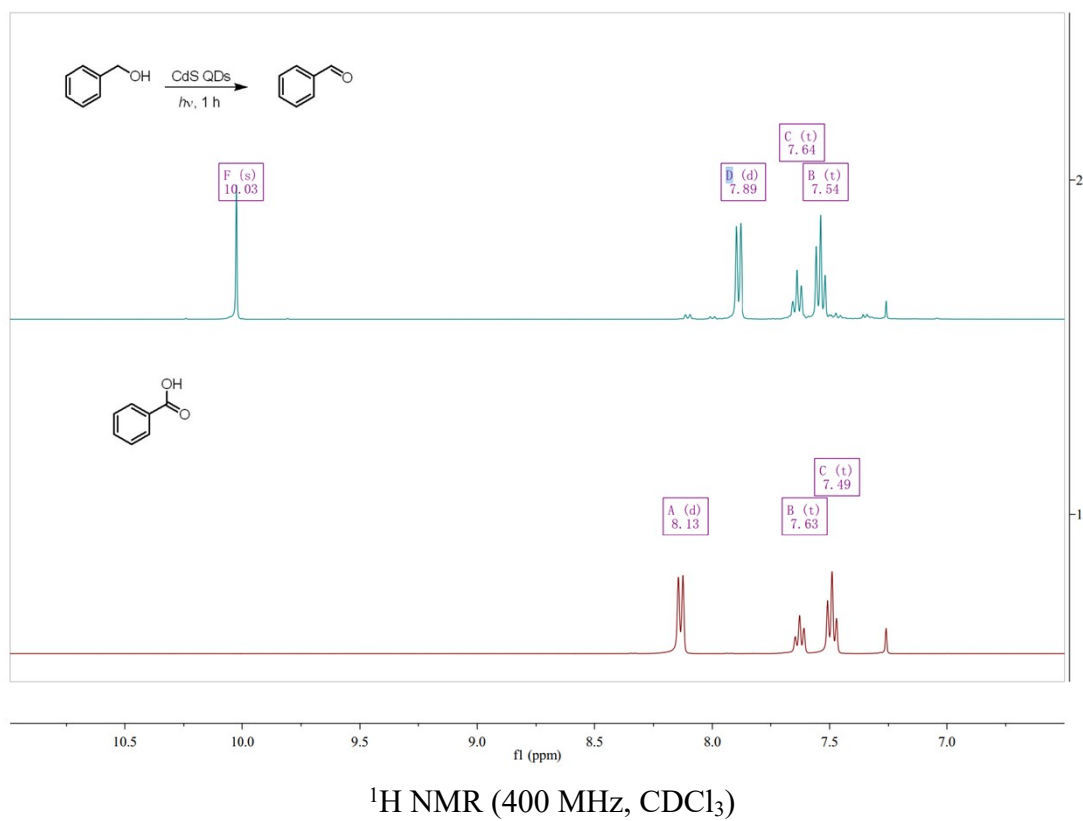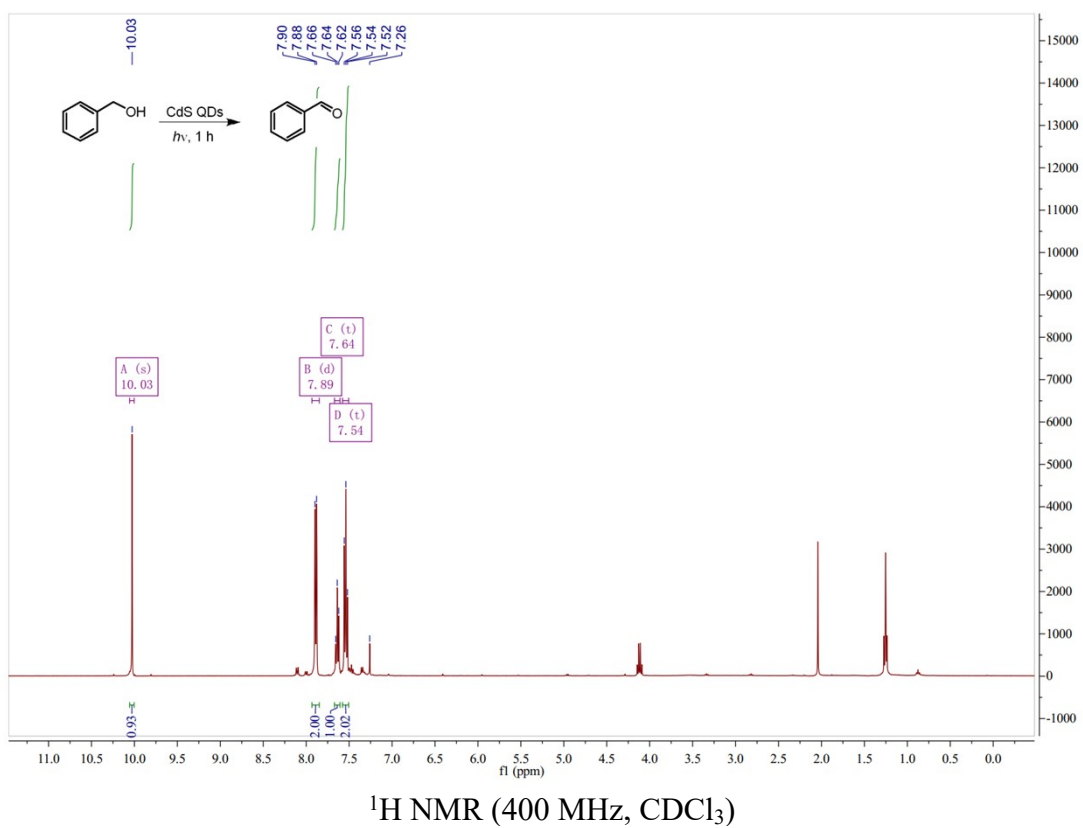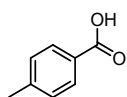
¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).
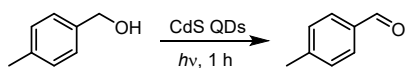
¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 1H), 7.78 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H).
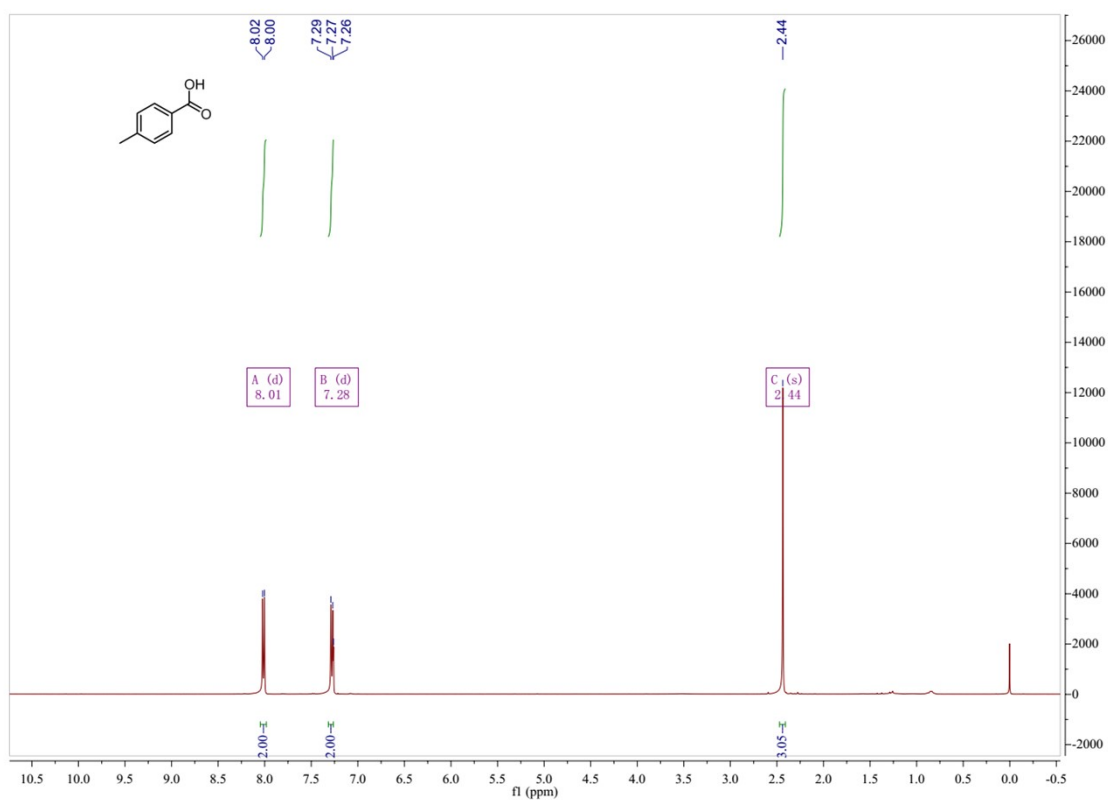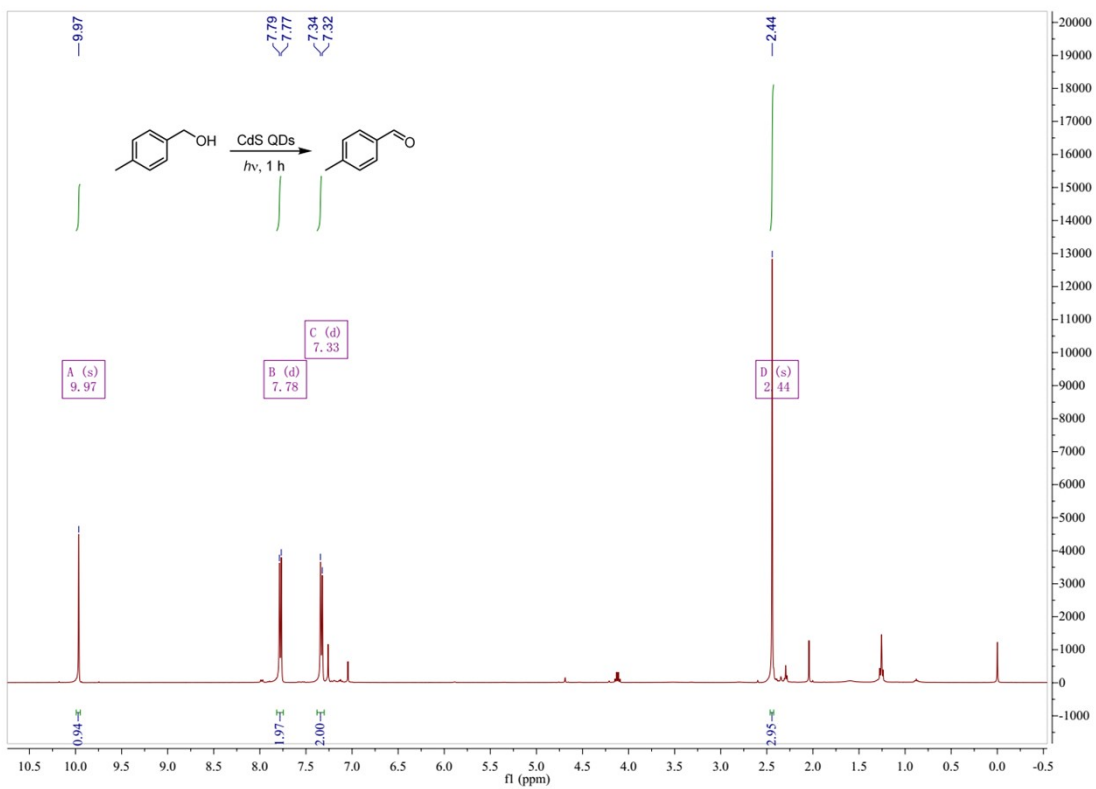
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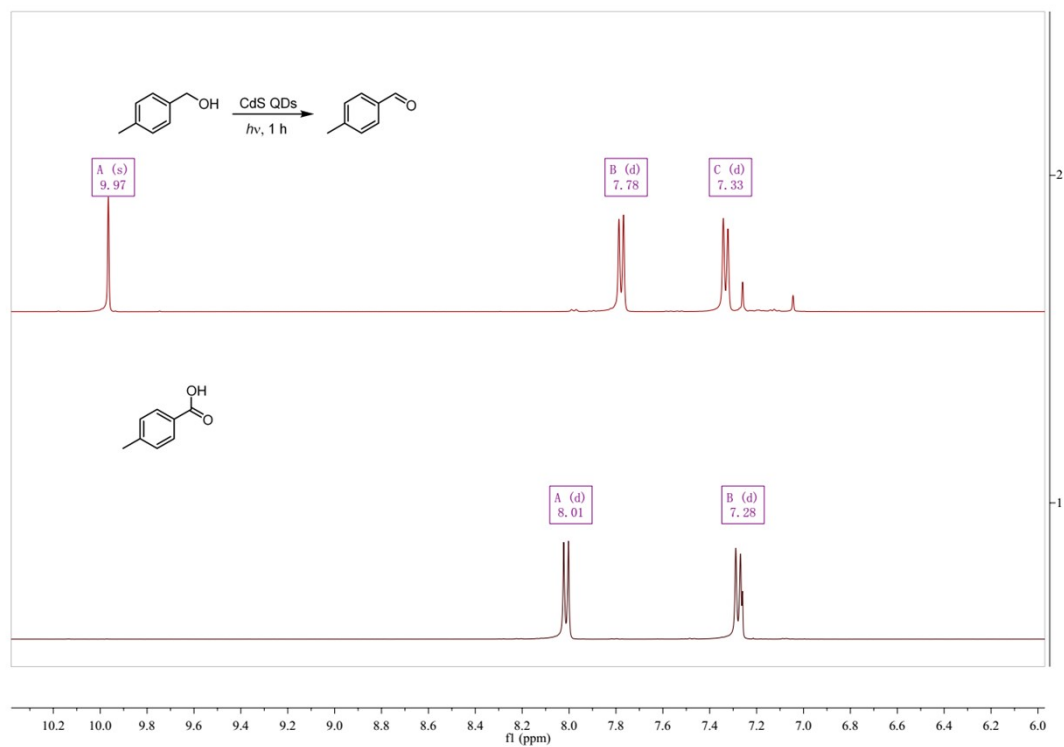
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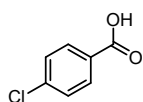
^{1}H NMR (400 MHz, CDCl$_3$)

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.15 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H).
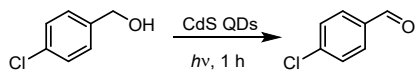
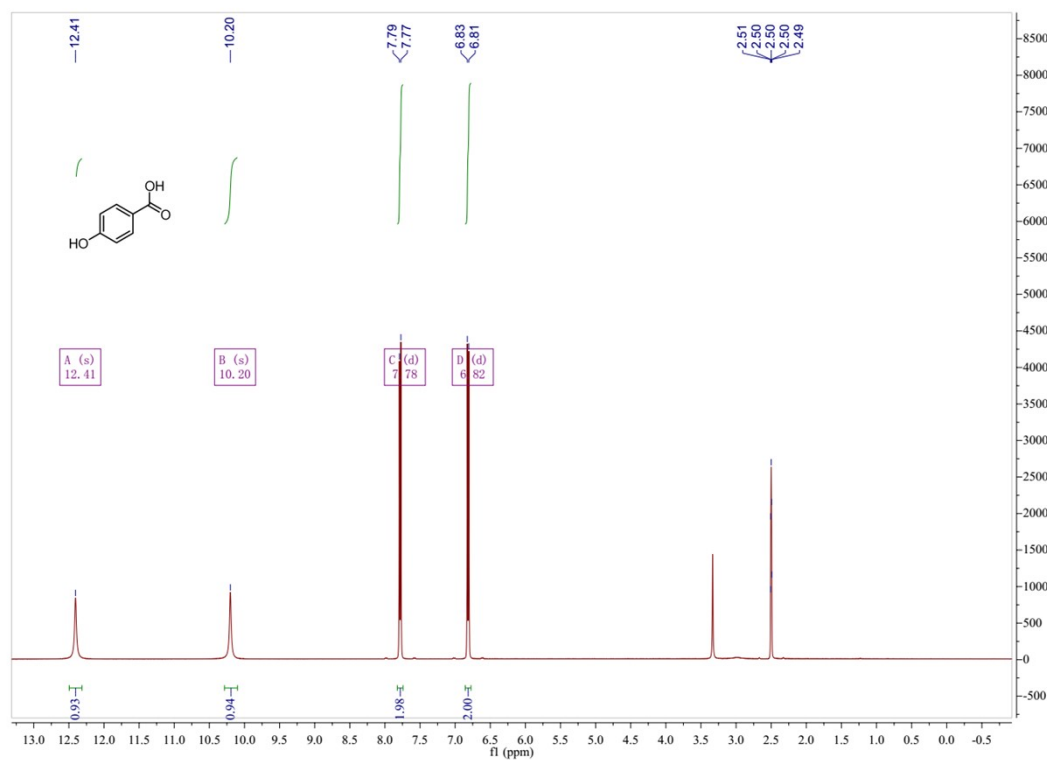**¹H NMR (400 MHz, DMSO-*d*₆)** δ 10.52 (s, 1H), 8.45 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 2H).
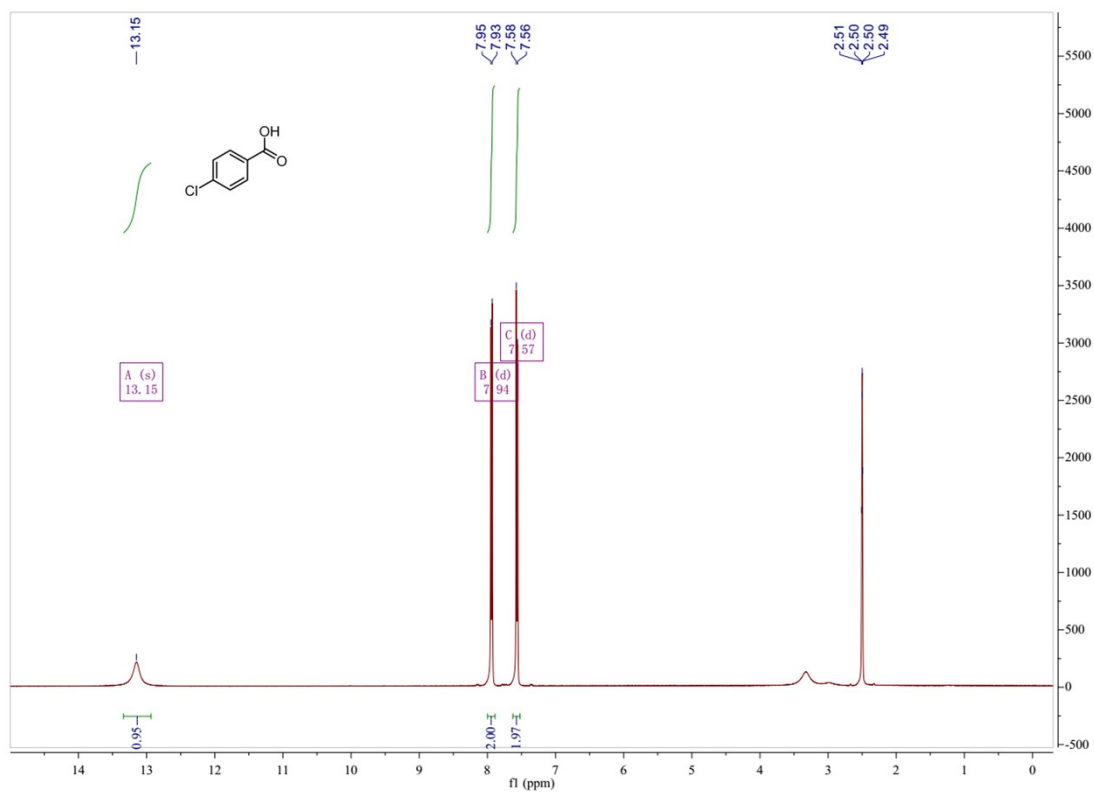
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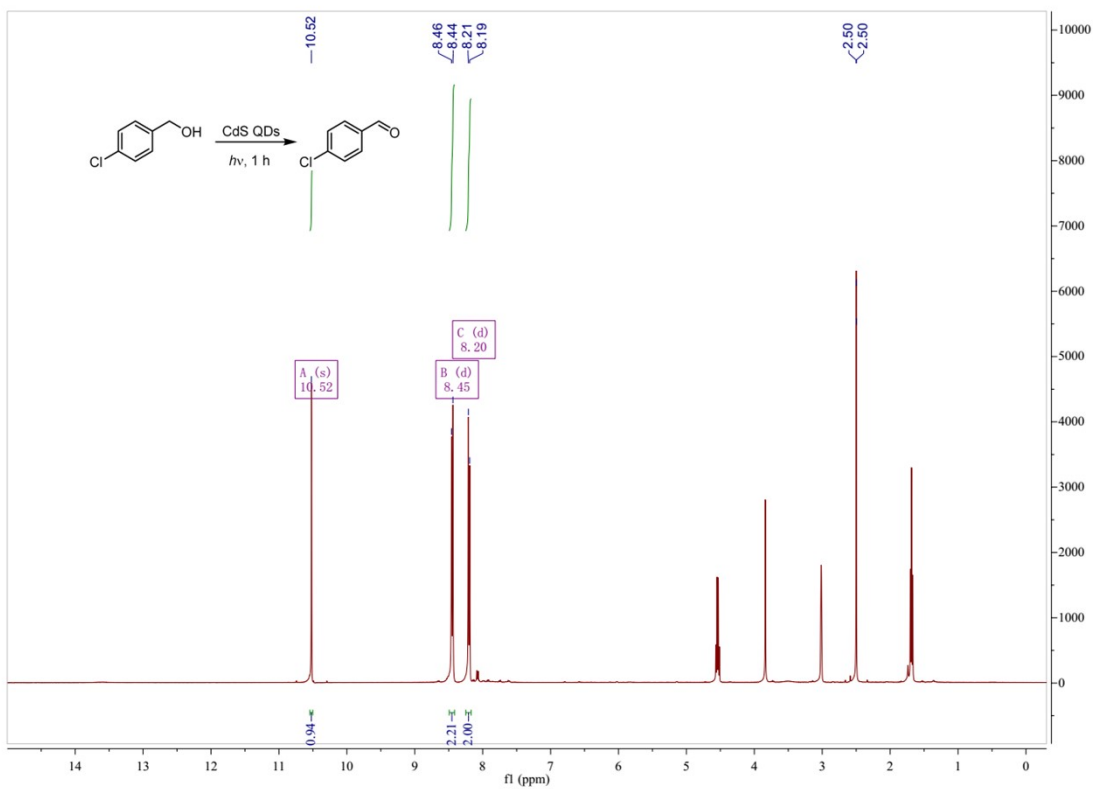
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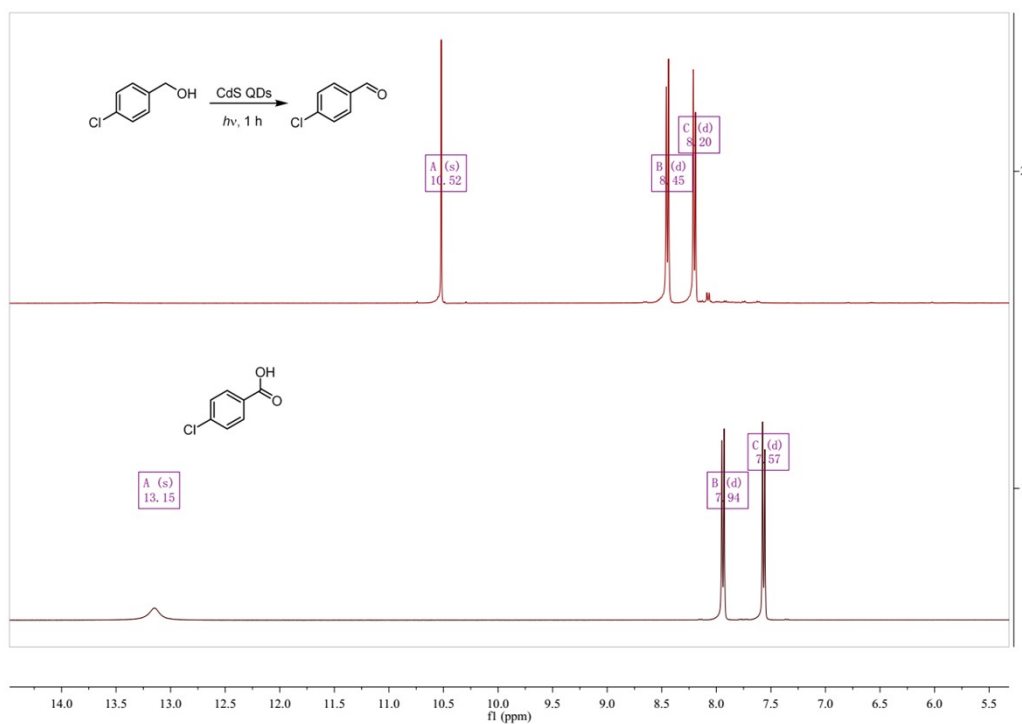
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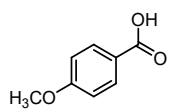
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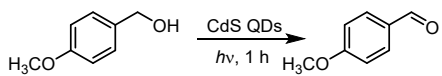
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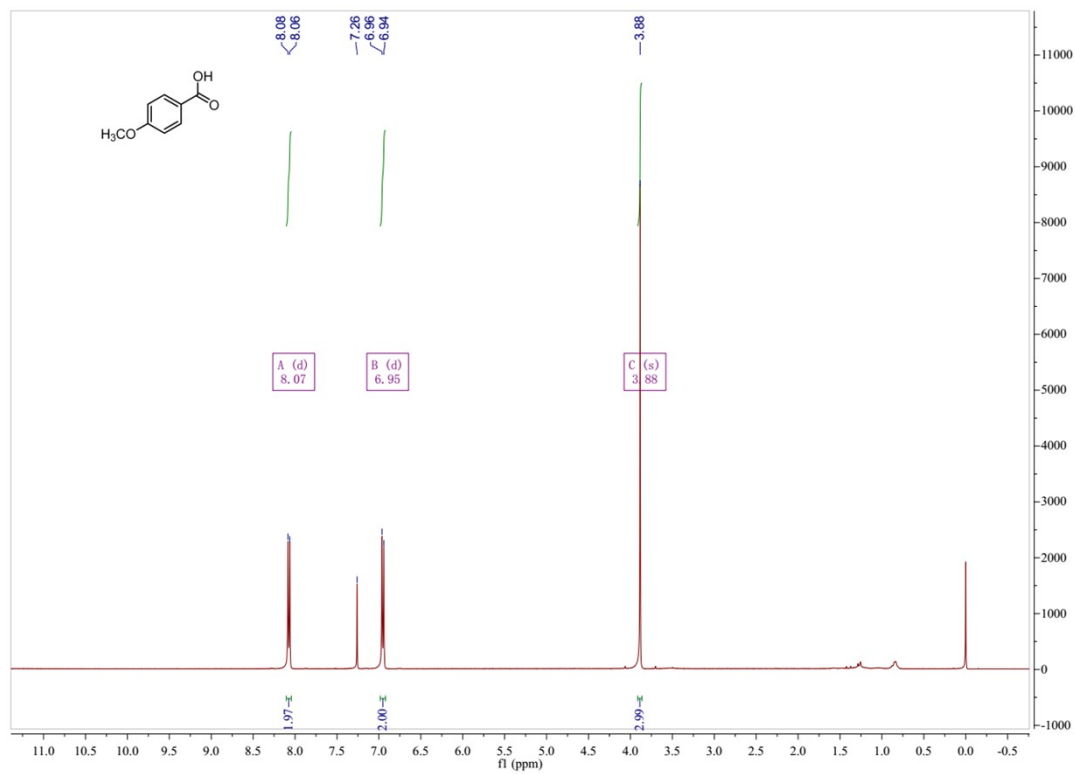
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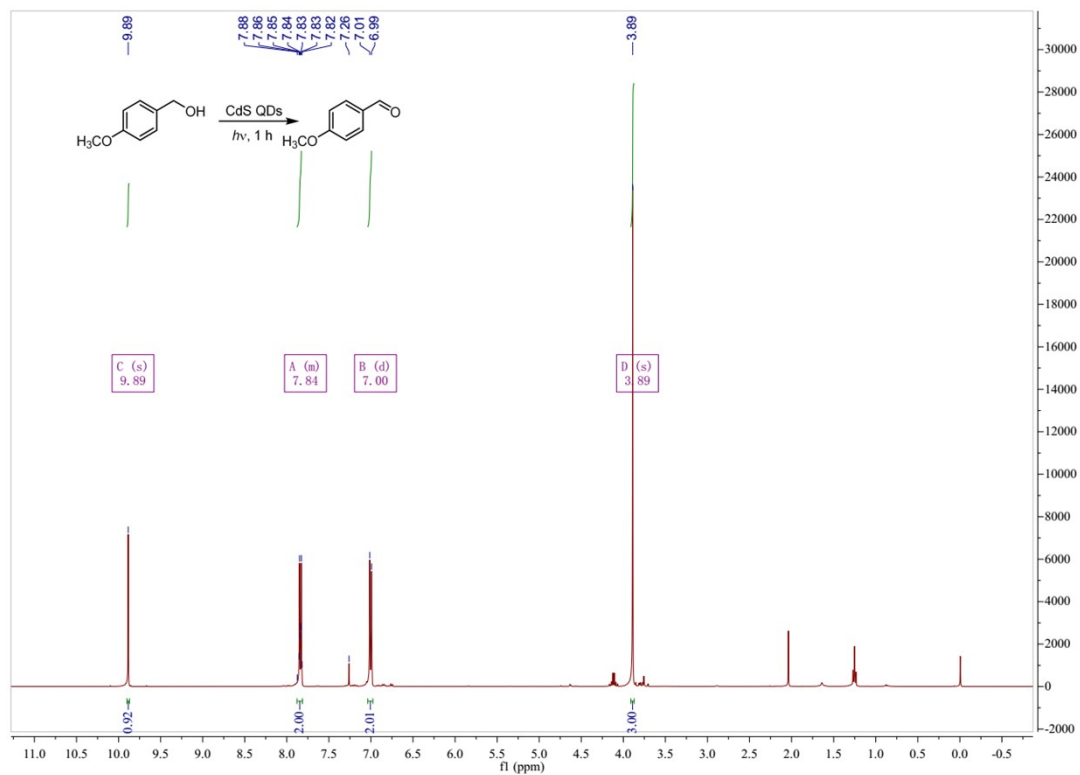
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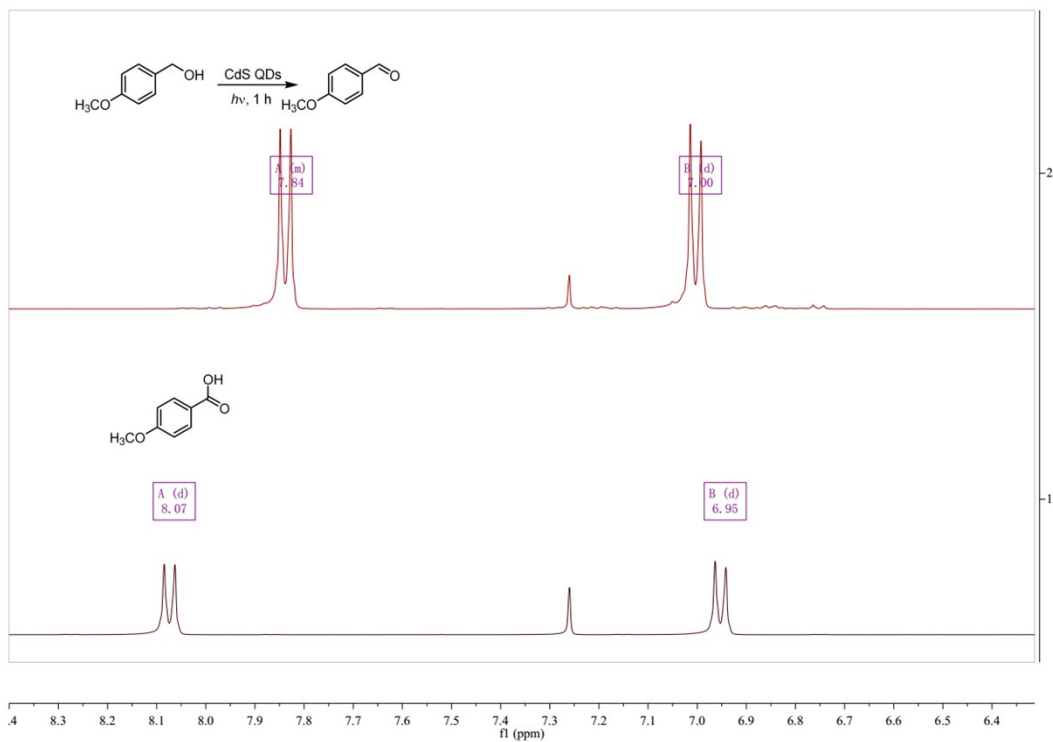
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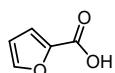
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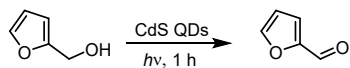
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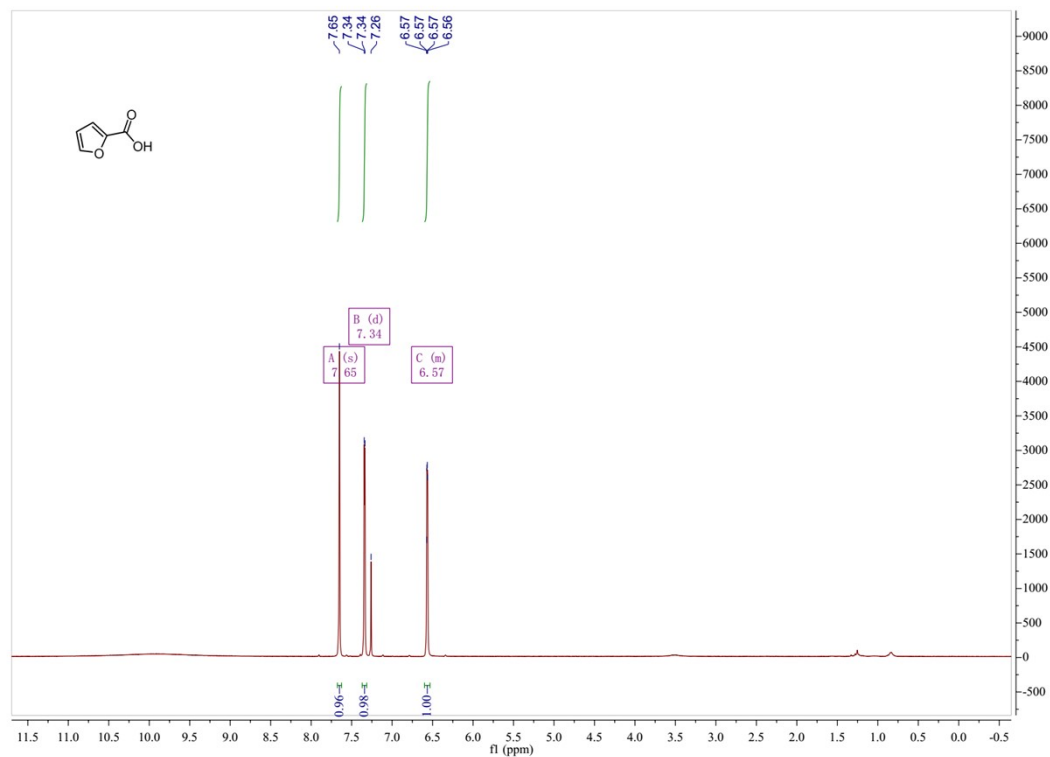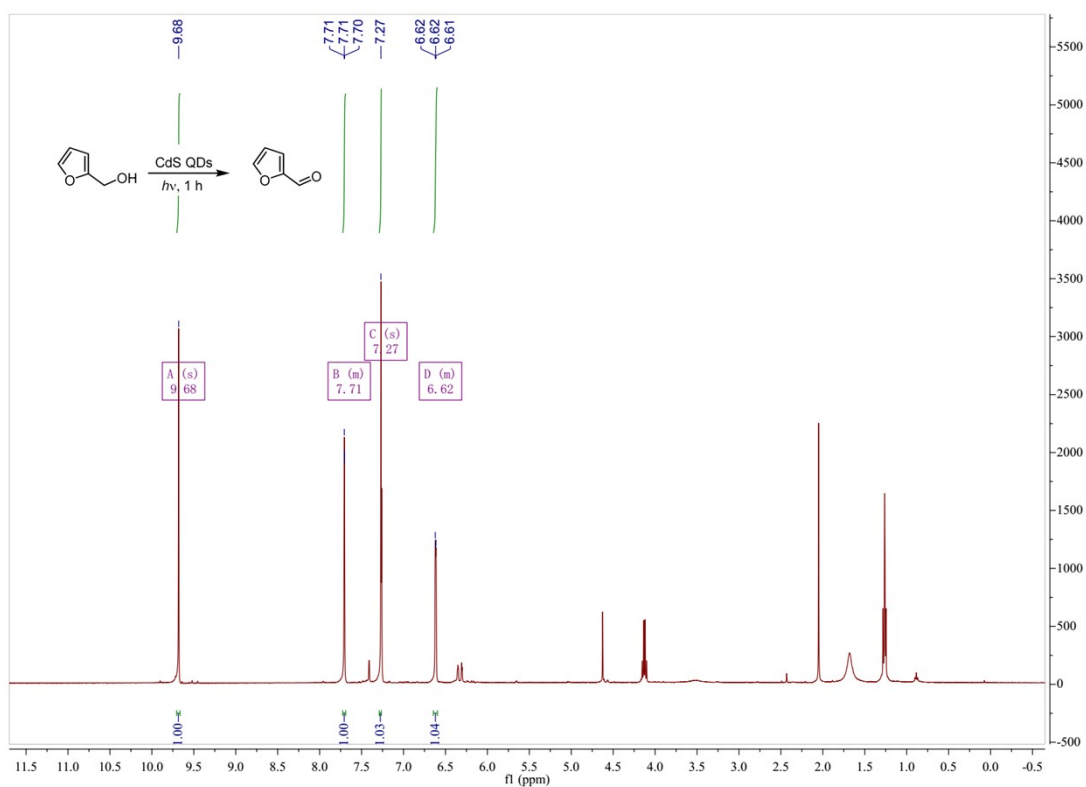
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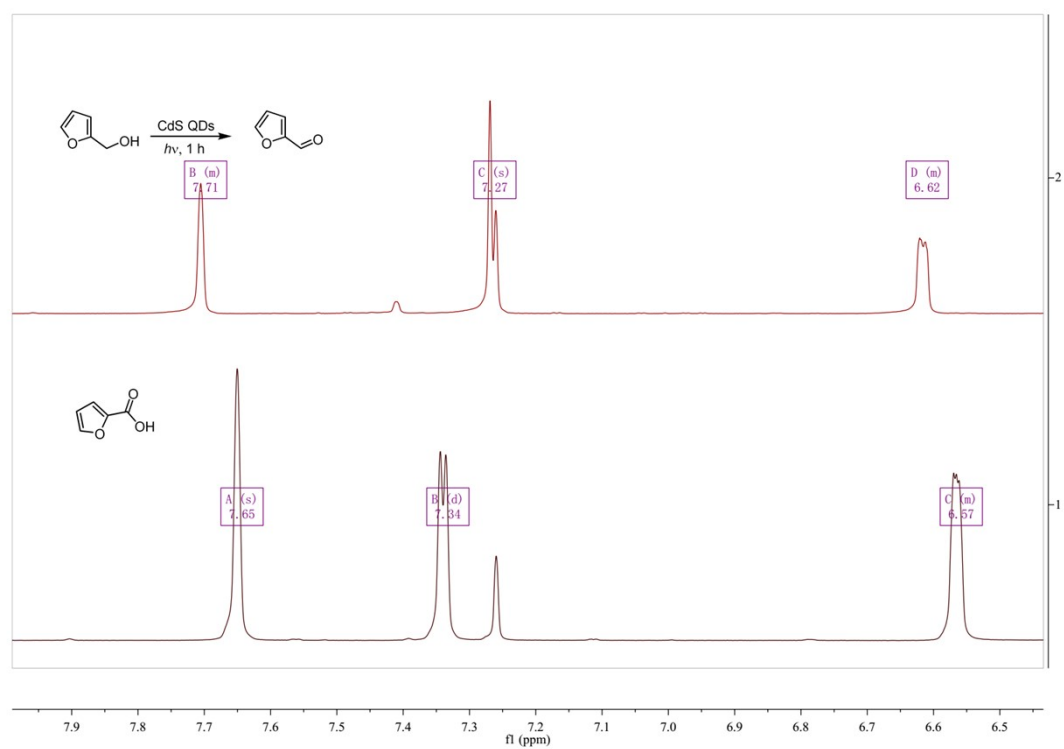
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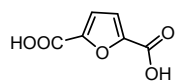
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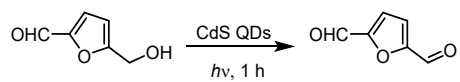
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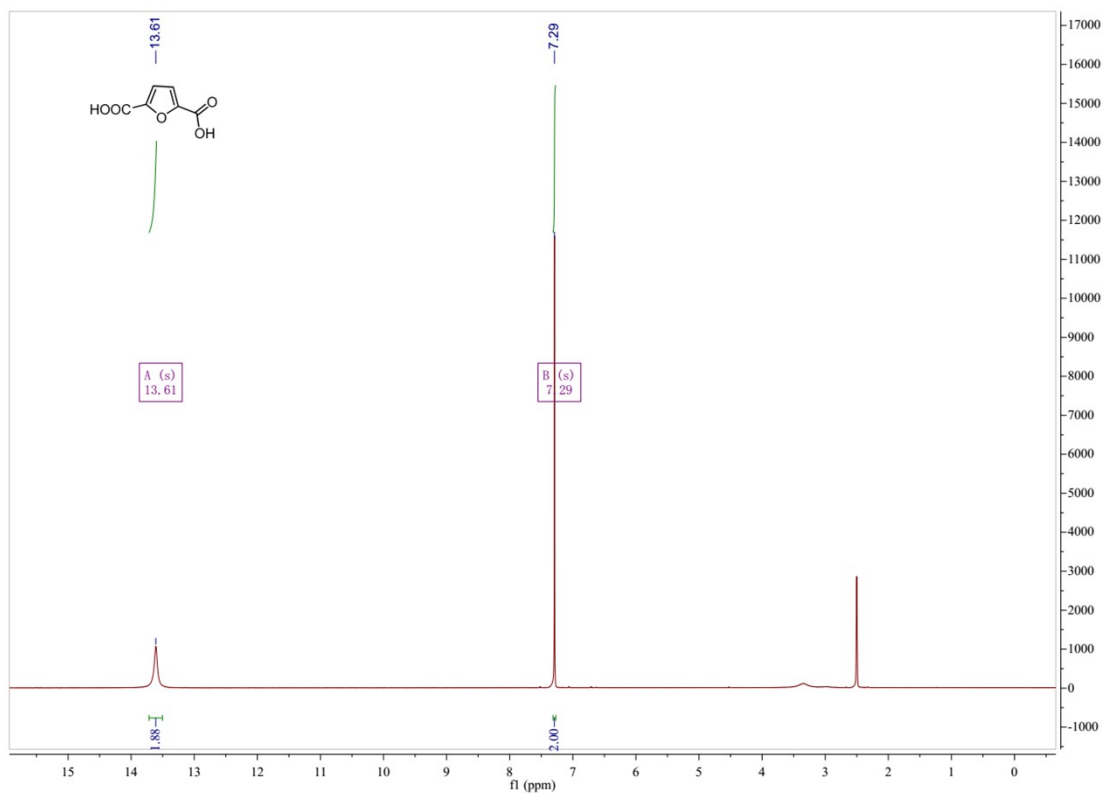
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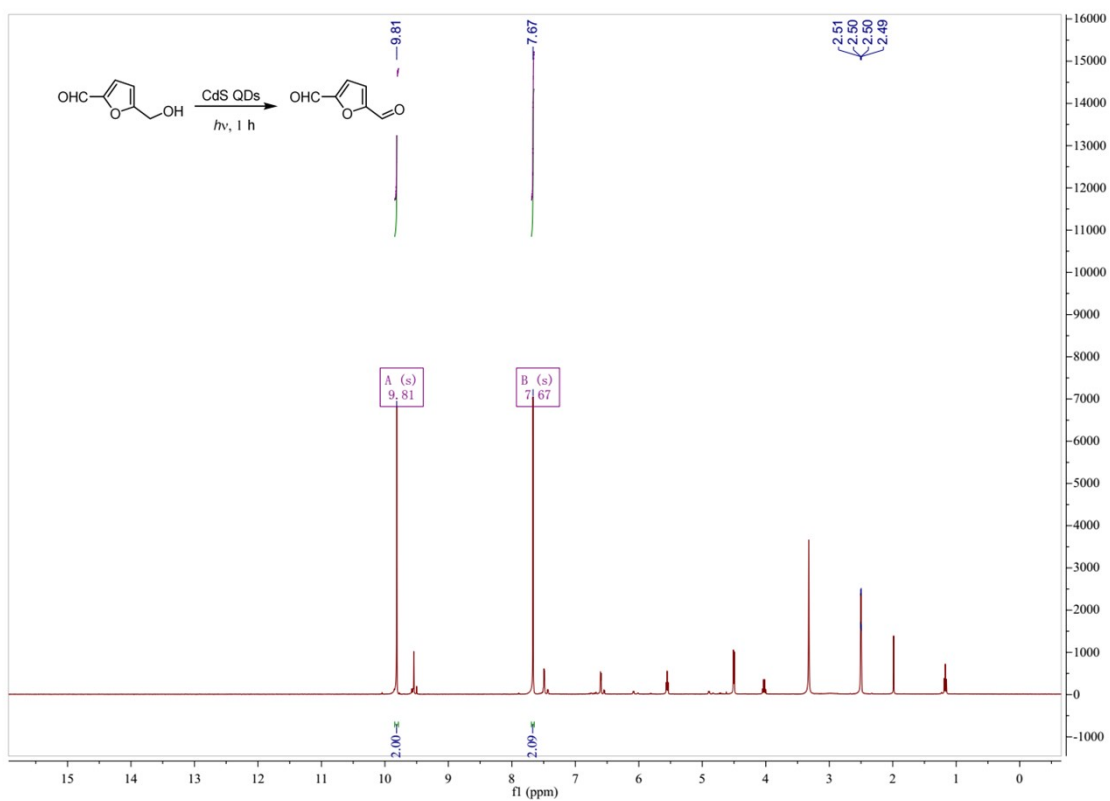
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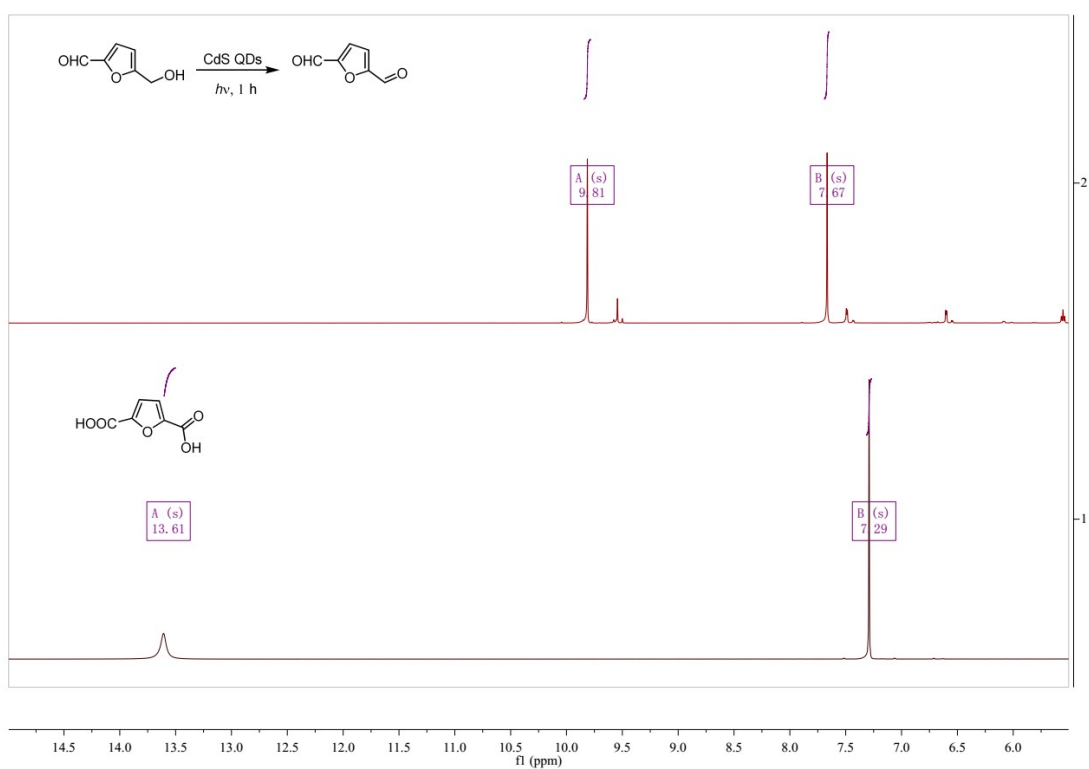
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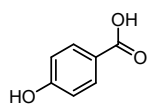
¹H NMR (400 MHz, DMSO-*d₆*) δ 12.41 (s, 1H), 10.20 (s, 1H), 7.78 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H).
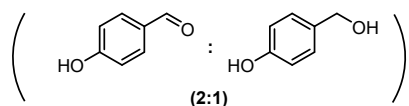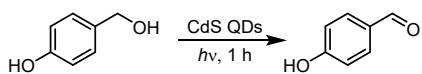
¹H NMR (400 MHz, DMSO-*d₆*, substituted benzaldehyde) δ 9.79 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H).
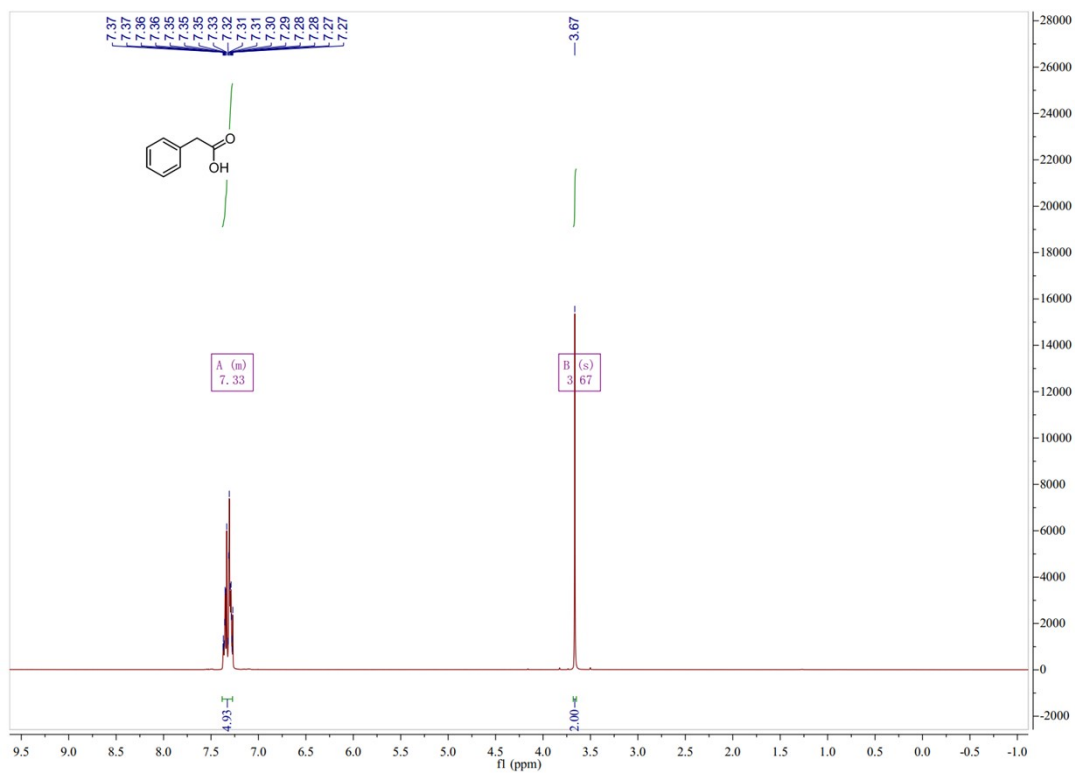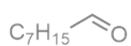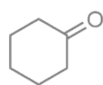
¹H NMR (400 MHz, DMSO-*d₆*, substituted benzyl alcohol) δ 7.09 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.1 Hz, 2H), 4.93 (s, 1H), 4.35 (s, 2H).

¹H NMR (400 MHz, DMSO-*d₆*)
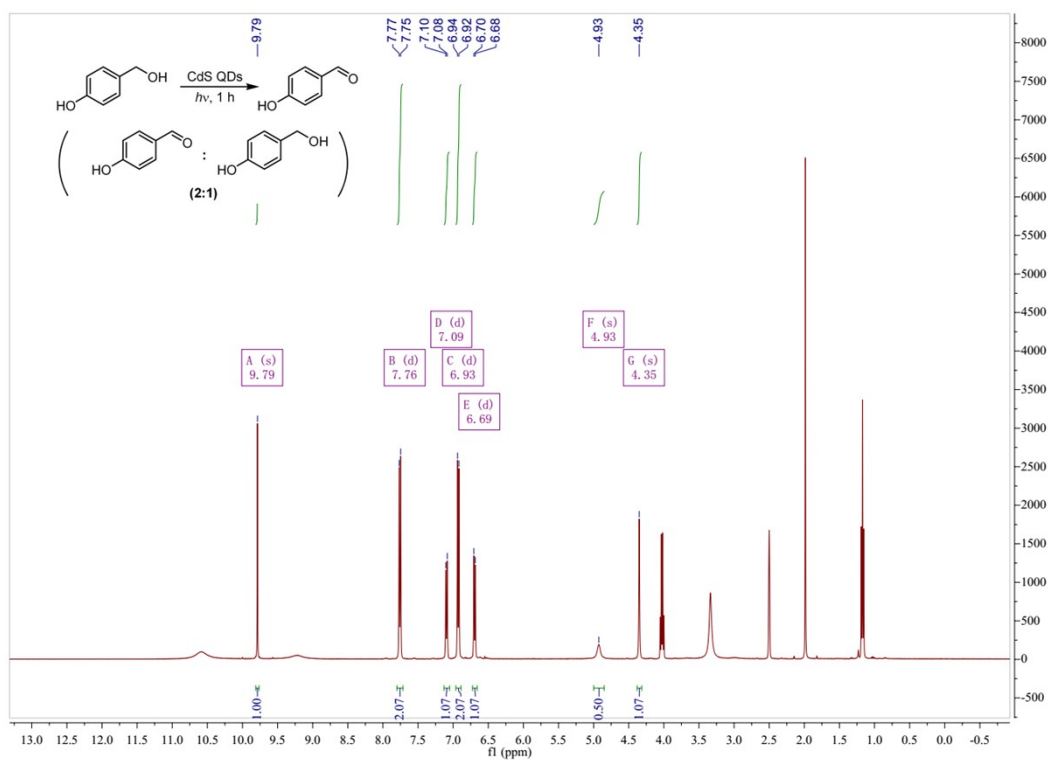
^{1}H NMR (400 MHz, DMSO-d_6)
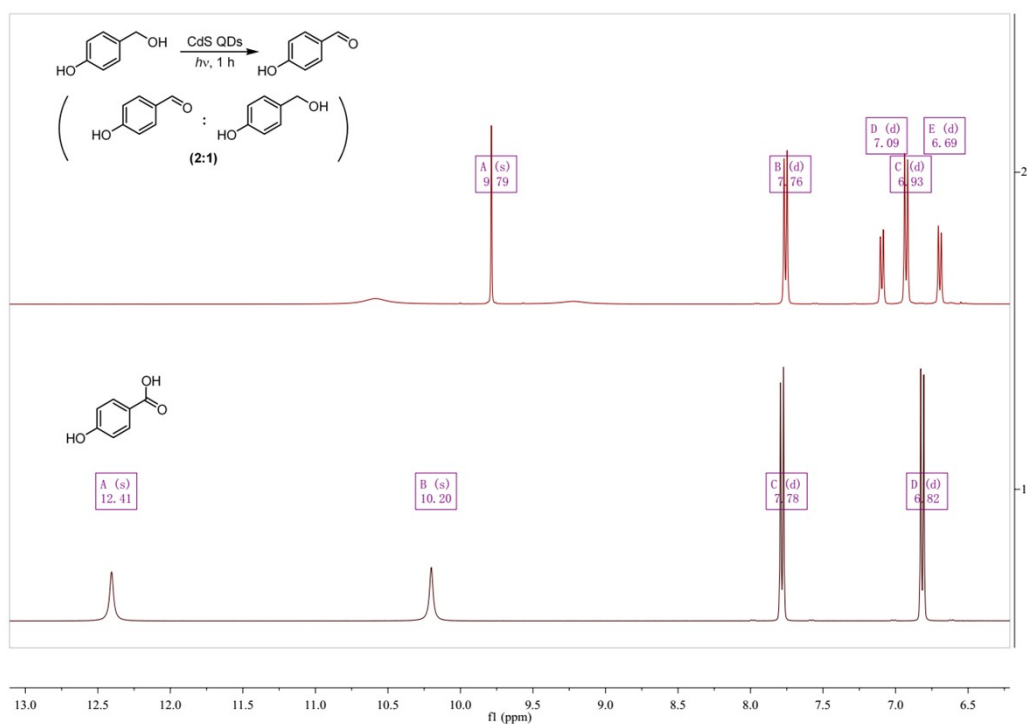
^{1}H NMR (400 MHz, DMSO-d_6)
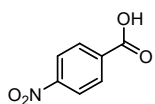
¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 8.7 Hz, 2H), 8.28 (d, J = 8.8 Hz, 2H).

(1.7:1)
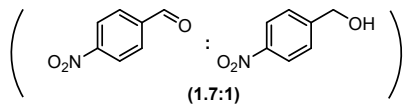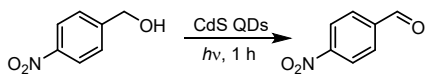
¹H NMR (400 MHz, CDCl₃, substituted benzaldehyde) δ 10.16 (s, 1H), 8.40 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.6 Hz, 2H).

¹H NMR (400 MHz, CDCl₃, substituted benzyl alcohol) δ 8.22 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 4.84 (s, 2H).
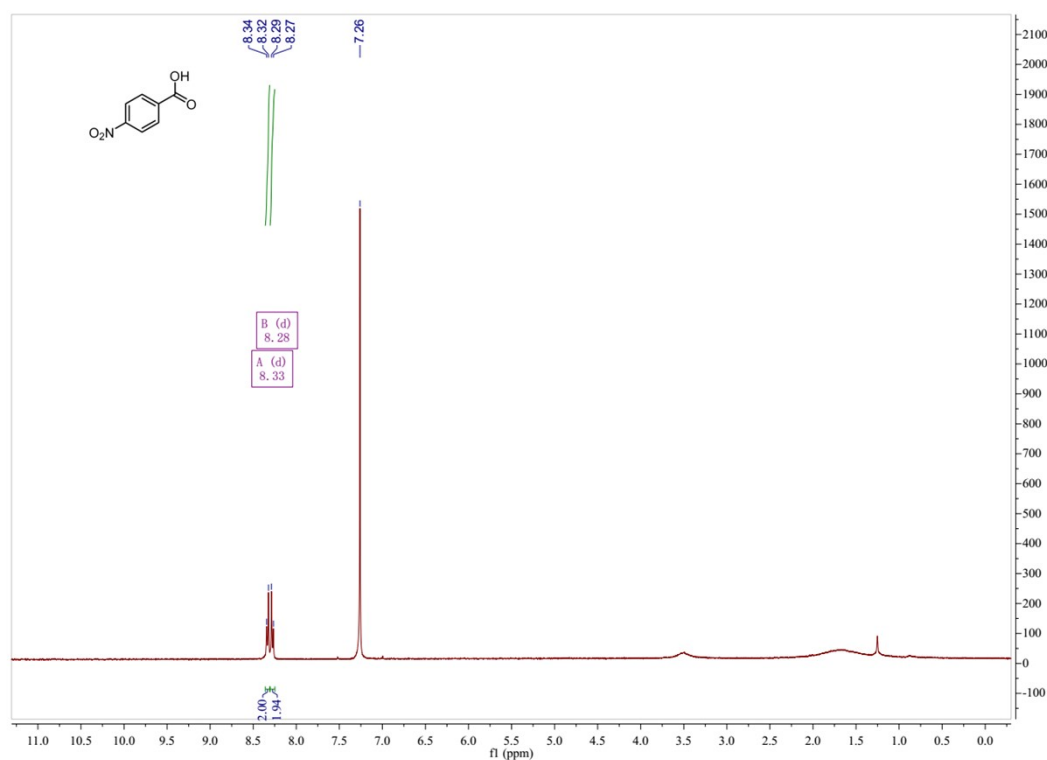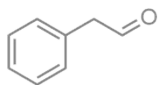

¹H NMR (400 MHz, CDCl₃)
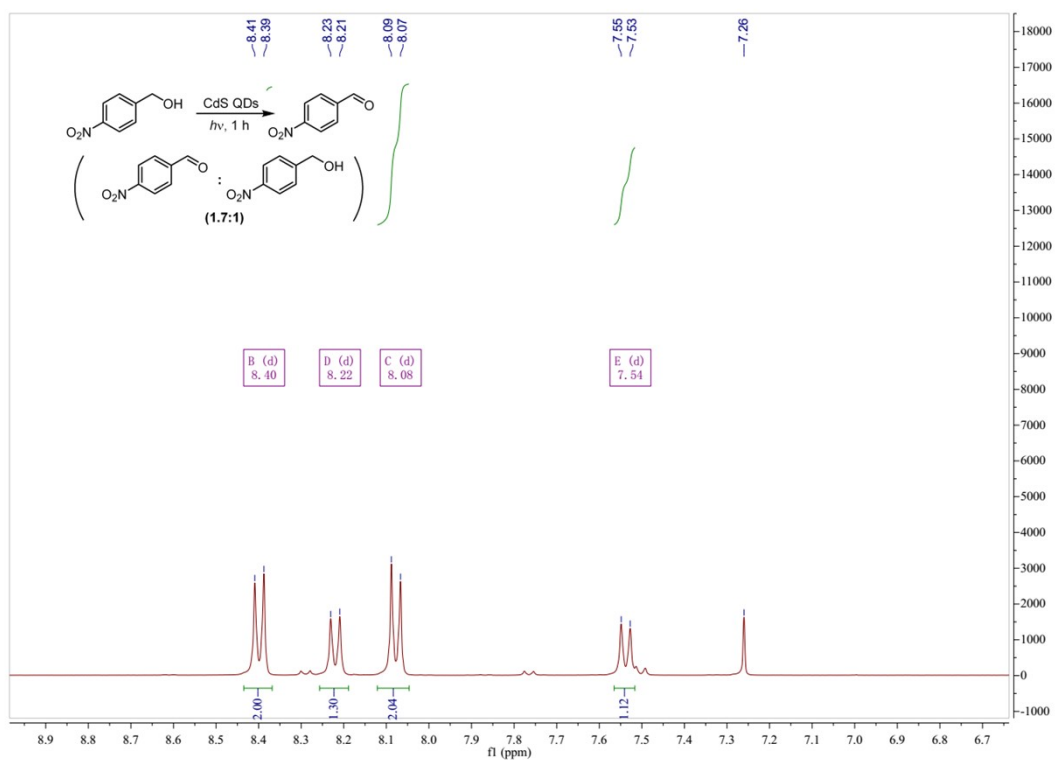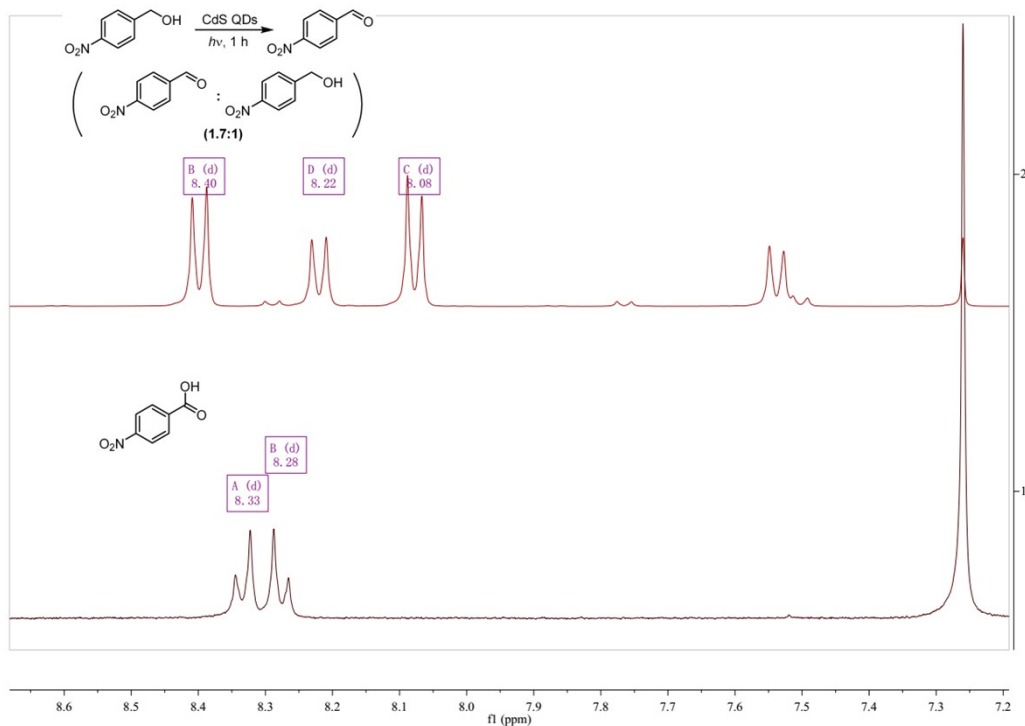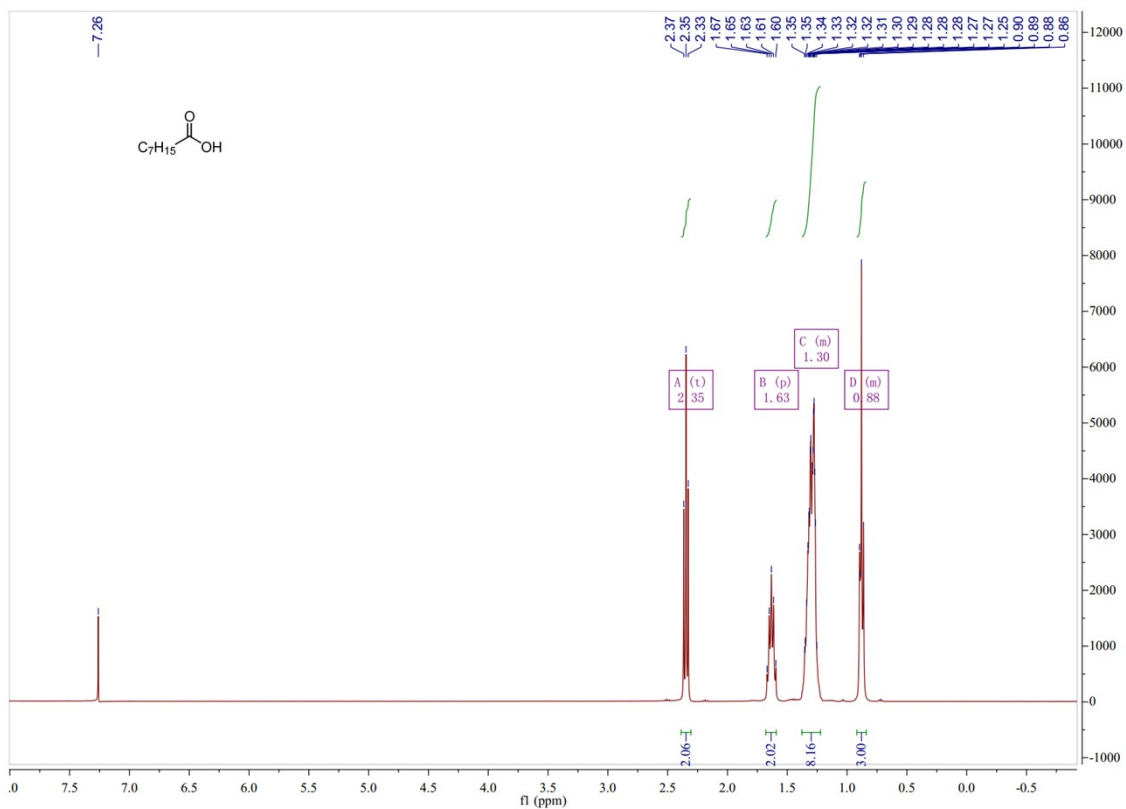
^{1}H NMR (400 MHz, CDCl$_3$)

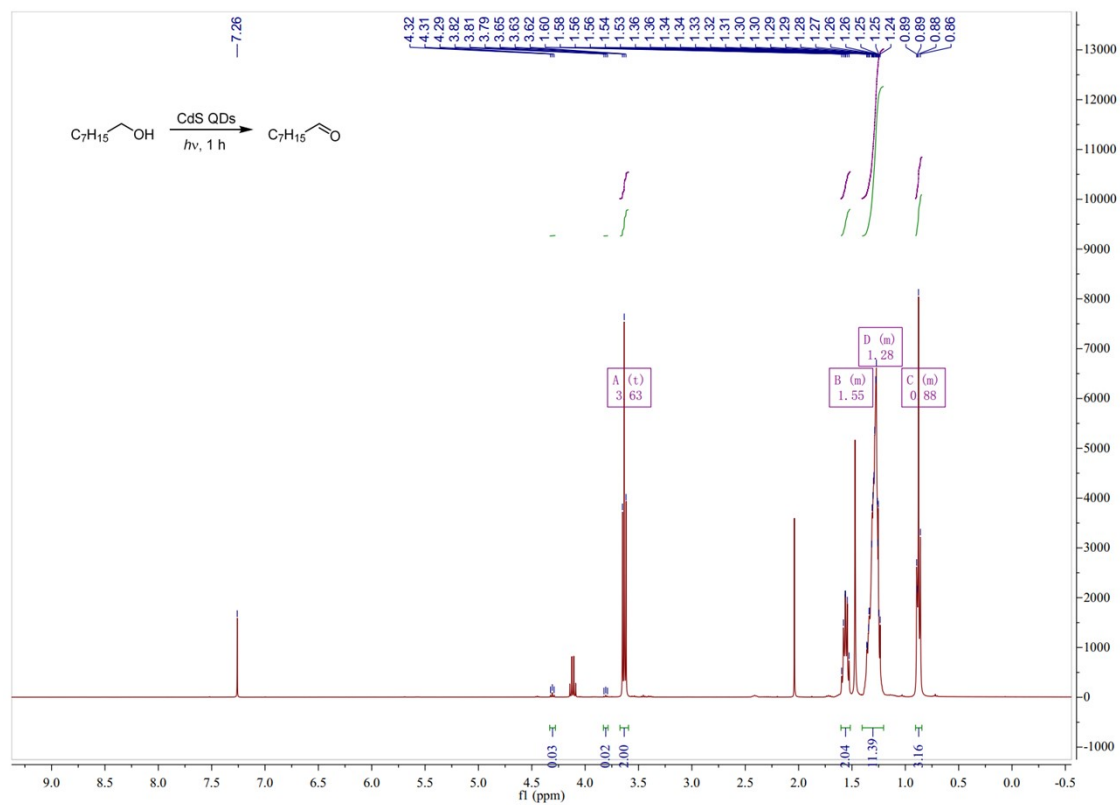^{1}H NMR (400 MHz, CDCl$_3$)

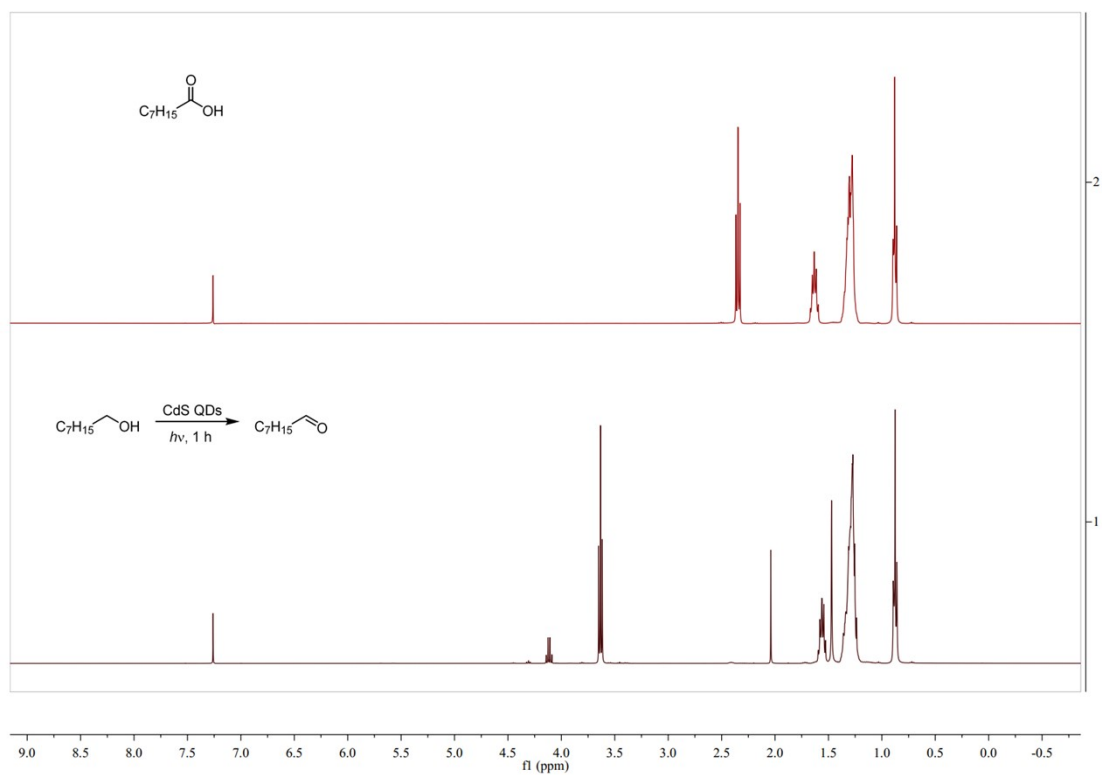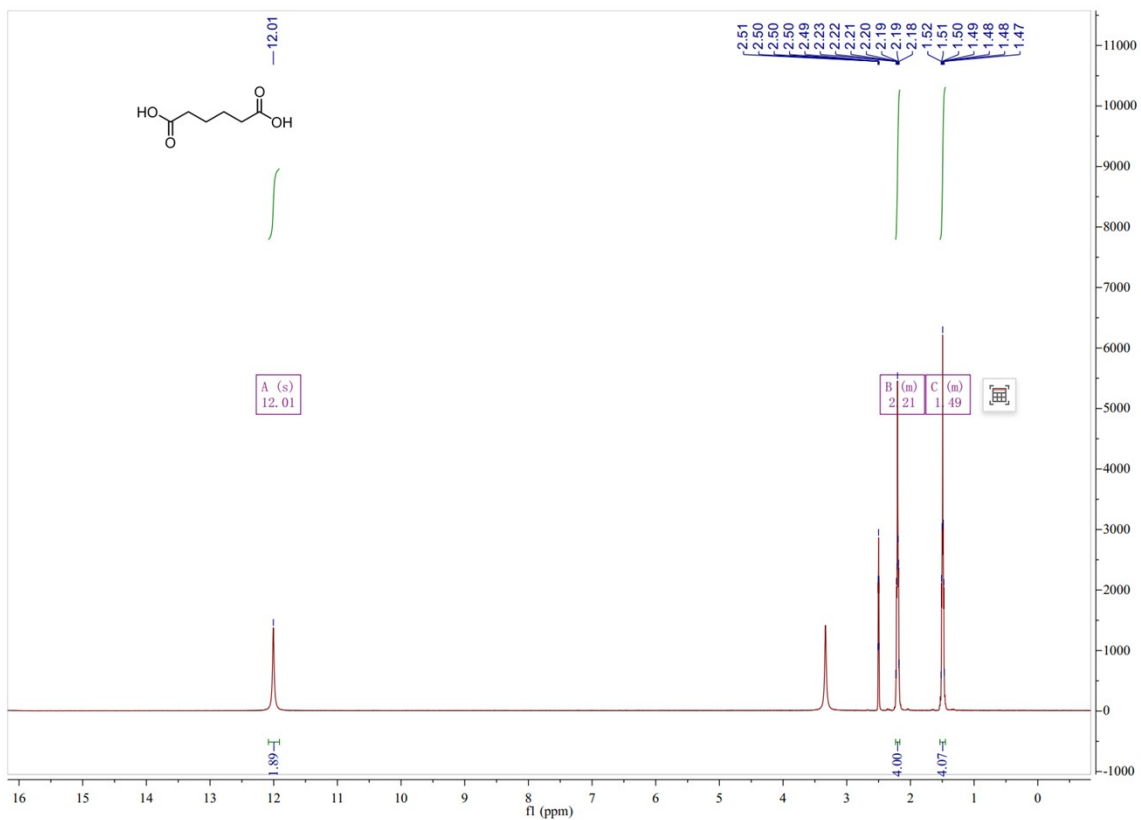**Not converted compounds**

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, CDCl$_3$)

^{1}H NMR (400 MHz, DMSO-d_6)

^{1}H NMR (400 MHz, DMSO-d_6)

^{1}H NMR (400 MHz, DMSO-d_6)