Supporting information for

Photocatalytic transfer hydrogenolysis of aryl ethers

Zhikun Peng [a,1], Zhixi Wu [a,1], Xiaotong Sun [b] and Hongji Li [b, *]

[a] *Henan Institutes of Advanced Technology, Zhengzhou University, No.100 Science Avenue, Zhengzhou, 450001 (China)*

[b] *Green Catalysis Center, and College of Chemistry, Zhengzhou University, No.100 Science Avenue, Zhengzhou, 450001 (China), E-mail:*

hongjili@zzu.edu.cn

[1] These authors contributed equally to this work.

Computational details

We performed the DFT calculations in the Vienna ab initio simulation package (VASP).[1] We adopted a spin-polarized GGA PBE functional, all-electron plane-wave basis sets with an energy cutoff of 520 eV, and a projector augmented wave (PAW) method.[2] We used a $(3 \times 3 \times 1)$ Monkhorst-Pack mesh for the Brillouin-zone integrations to be sampled. We used the conjugate gradient algorithm during the optimization. The convergence threshold was set as $1*10^{-5}$ eV in total energy and 0.02 eV/Å in force on each atom. In the simulations, we employed a non-periodic boundary condition. H atoms doping in the Pt(111) structure were formed. The energy minimization was performed to find the thermal stable morphology and achieve a conformation with minimum potential energy. And these minimum energy conformations were used as initial states in the following electronic structure simulations.

The adsorption energy change (ΔE_{abs}) was determined as follows:

$$\Delta E_{abs} = E_{total} - E_{slab} - E_{mole}$$

where E_{total} is the total energy for the adsorption state, E_{slab} is the energy of pure surface, E_{mole} is the adsorption energy of molecule.

The free energy change (ΔG) for adsorptions were determined as follows:

$$\Delta G = E_{total} - E_{slab} - E_{mole} + \Delta E_{ZPE} - T\Delta S$$

where E_{total} is the total energy for the adsorption state, E_{slab} is the energy of pure surface, E_{mole} is the adsorption energy of molecule, ΔE_{ZPE} is the zero-point energy change and ΔS is the entropy change.

The preparation of substrates

The synthesis of (cyclohexyloxy)benzene
A 100 mL flask equipped with a stir bar was loaded with phenol (5 mmol), cyclohexene (20 mmol) and anhydrous toluene (1 mL). After stirring for 5 min, the triflic acid (10 μL) was added before sealing. The mixture was heated at 85 °C for 11 h. After reaction, the toluene was removed in vacuo. The sample was loaded onto silica gel and subjected to flash column chromatography (dichloromethane : petroleum ether = 1:6) to give pure products. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.29 – 7.22 (m, 2H), 6.95 – 6.86 (m, 3H), 4.34 – 4.07 (m, 1H), 1.99 (m, 2H), 1.80 (m, 2H), 1.52 (m, 3H), 1.43 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 157.80, 129.42, 120.48, 116.09, 75.37, 31.88, 25.67, 23.83.

The synthesis of 1-(Cyclohexyloxy)-4-methylbenzene
The synthesis of 1-(Cyclohexyloxy)-4-methylbenzene was similar with that of (cyclohexyloxy)benzene except for utilizing 4-methylphenol as the nucleophile. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.05 (d, J=8.1, 2H), 6.80 (d, J=8.6, 2H), 4.25 – 4.10 (m, 1H), 2.27 (s, 3H), 1.97 (d, J=10.6, 2H), 1.79 (d, J=5.1, 2H), 1.62 – 1.43 (m, 3H), 1.33 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 155.59, 129.87, 116.18, 75.66, 31.91, 25.69, 23.85, 20.49.
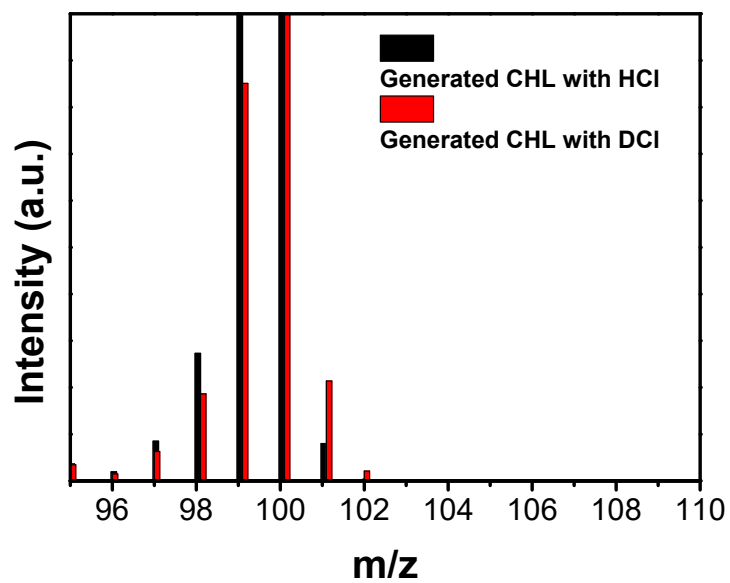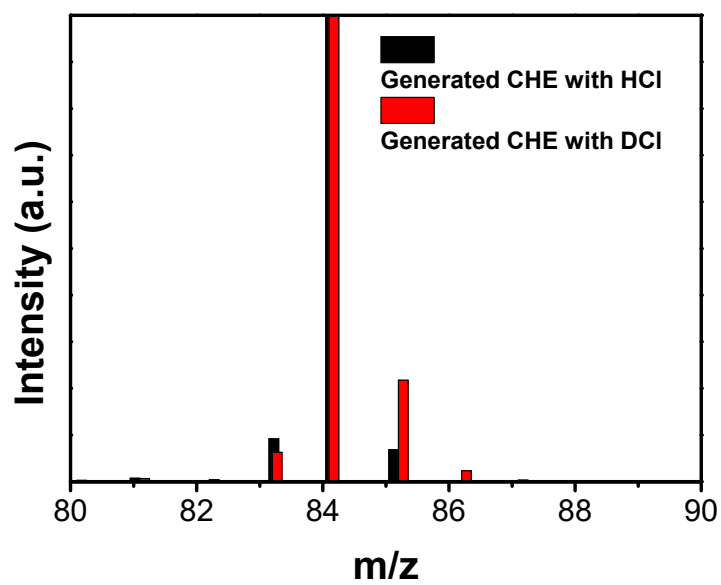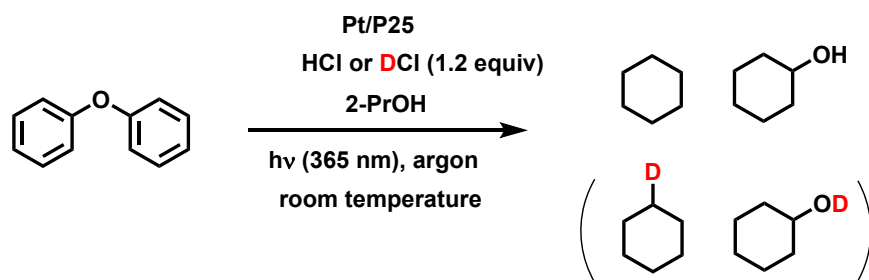
Other controlled experiments

Figure S1. Mass spectra analysis of controlled experiments using HCl and DCl.
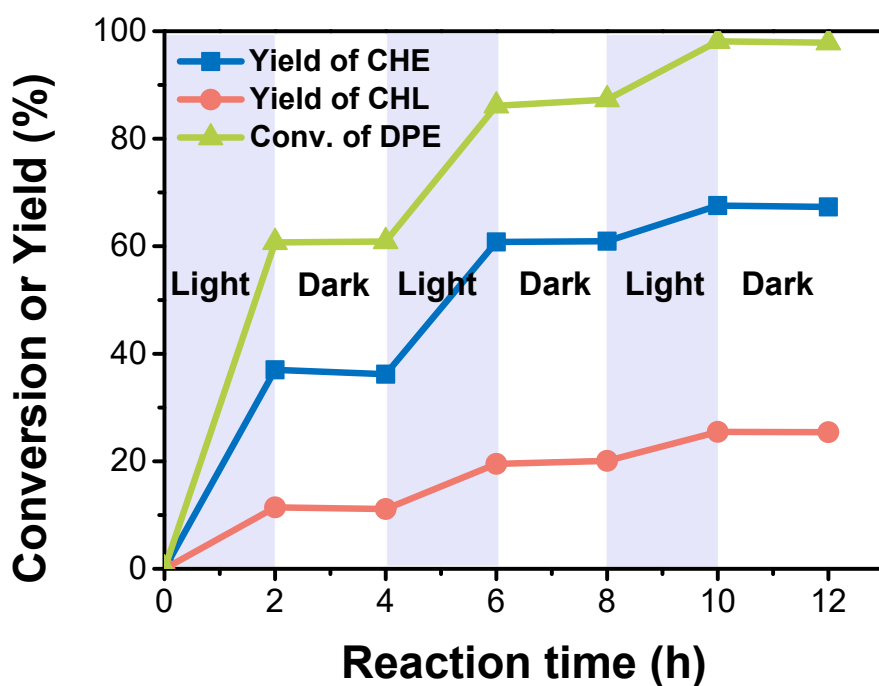
Figure S2. Switching on and off the light during photocatalytic transfer hydrogenolysis of diphenyl ether.
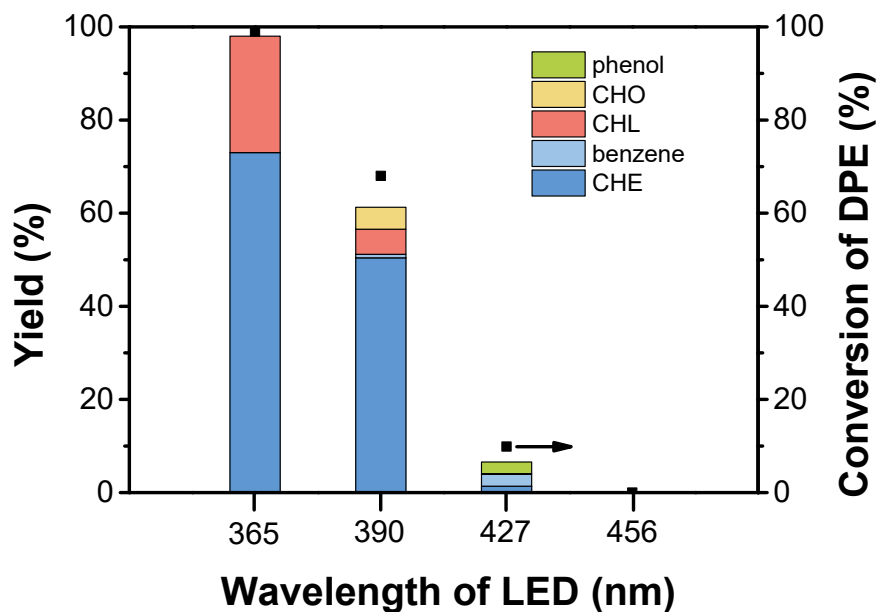

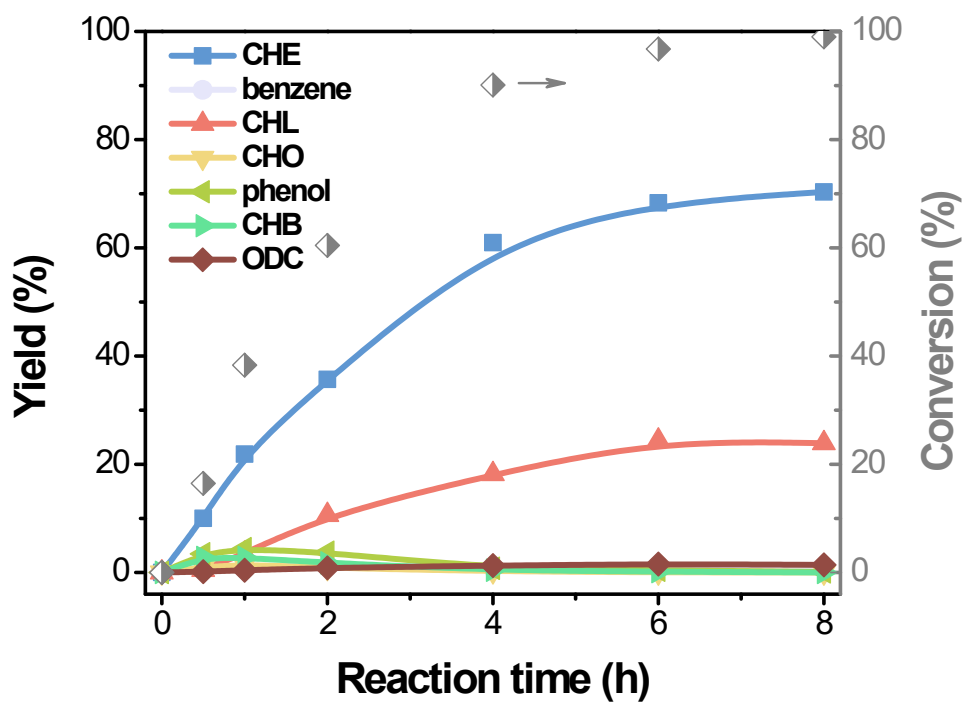**Figure S3.** The photocatalytic transfer hydrogenolysis of DPE using different LEDs.

Figure S4. Time course of reductive cleavage of diphenyl ether on Pt/P25.
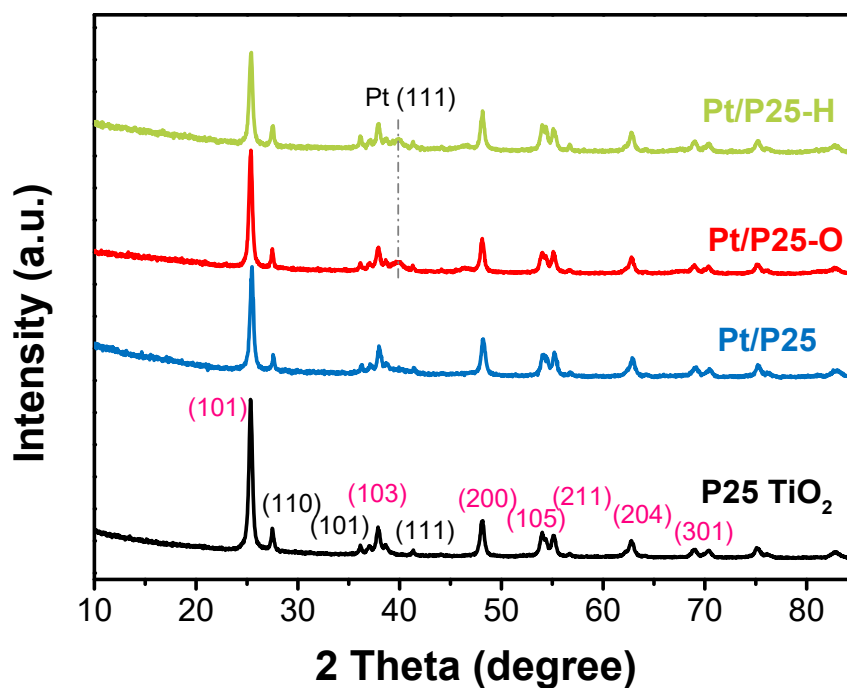

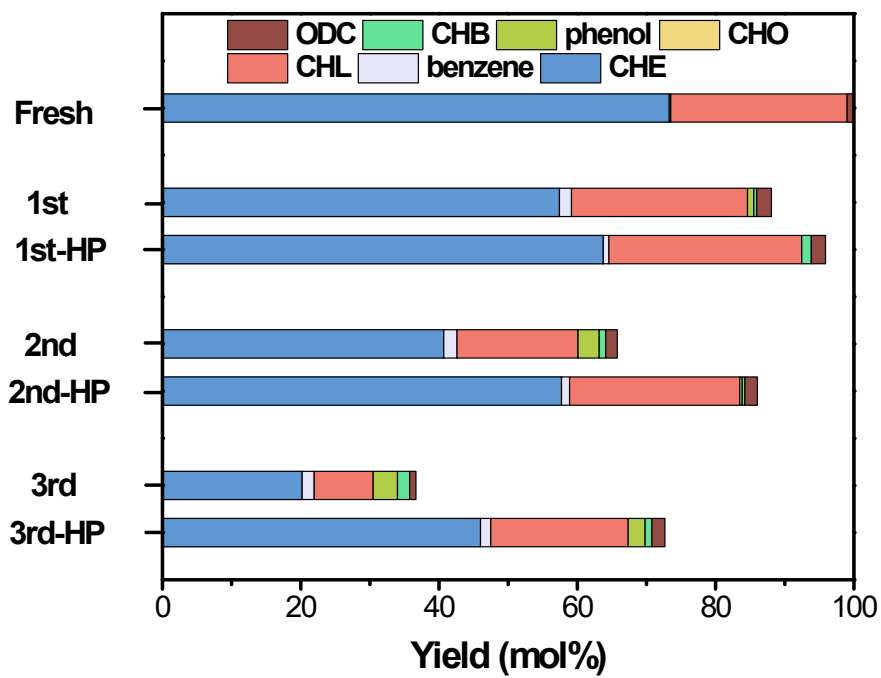**Figure S5.** XRD patterns of Pt/P25 catalysts.

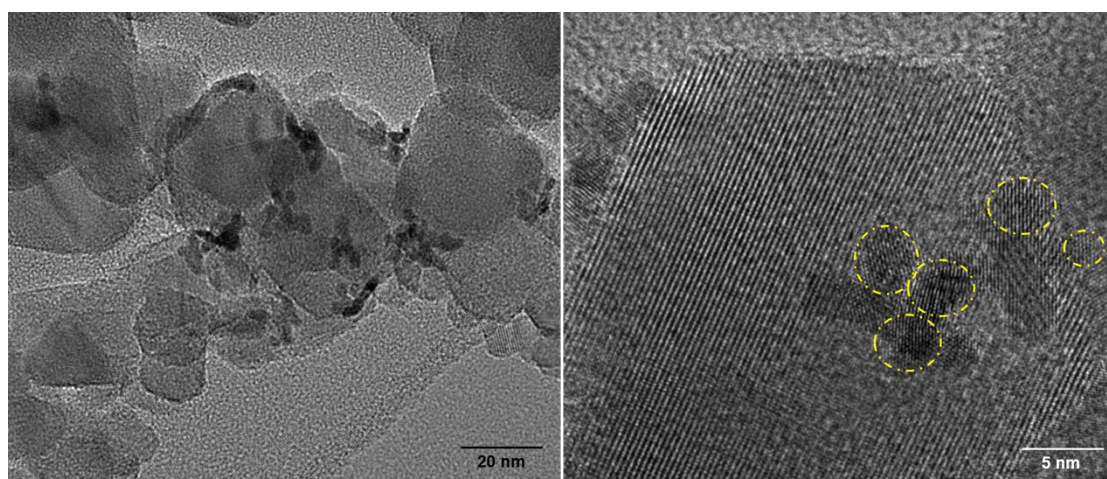**Figure S6.** Catalyst recycling tests. HP, heat treatment at 350 °C in air.

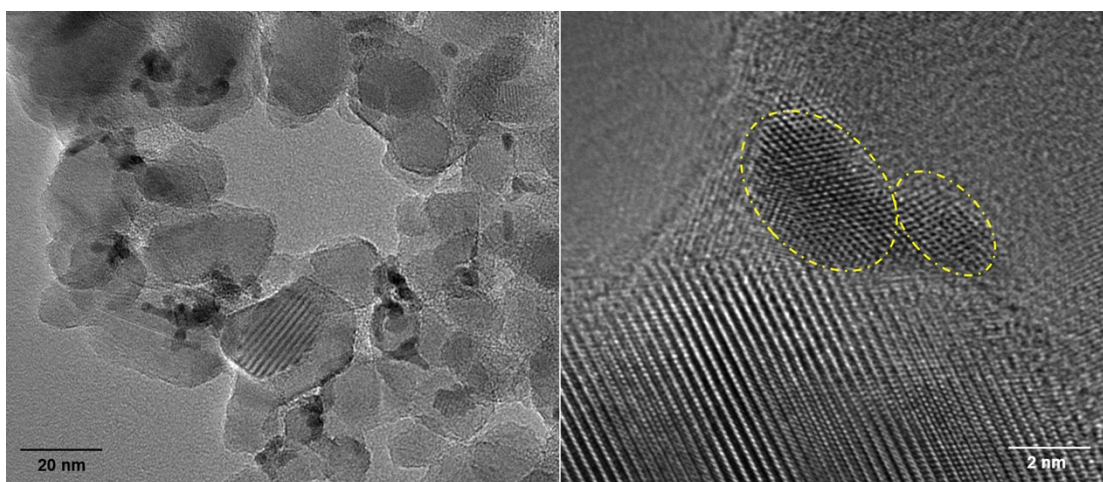**Figure S7.** TEM analysis of 3rd Pt/P25.

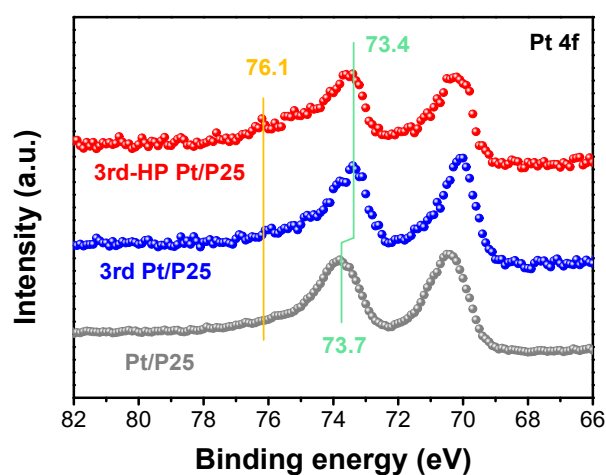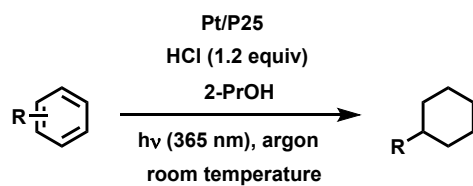**Figure S8.** TEM analysis of 3rd-HP Pt/P25.

Figure S9. Pt 4f XPS analysis of 3rd Pt/P25 and 3rd-HP Pt/P25.

The cycling stability of Pt/P25 was investigated (Figure S4). The gradual deactivation was observed after each cycling of Pt/P25, and partial reactivation can be achieved via heat treatment at 350 °C in air. TEM and XPS were used to reveal the changes of Pt species after cycling. No obvious growth of Pt particles was observed for 3rd Pt/P25 (Figure S5), even after the heat treatment (Figure S6). However, XPS analysis indicated that the binding energy of Pt $4f_{5/2}$ decreased after cycling (Figure S7), suggesting the reduction of Pt particles. As discussed in the catalytic performance of Pt/P25-H, the reduction of Pt particles may induce deactivation. Heat treatment in air generated more positive Pt species (76.1 eV) which may induce the reactivation. As discussed in the catalytic performance of Pt/P25-O, the coexistence of Pt^0 and $Pt^{\delta+}$ species was vital for the performance in hydrogen transfer.

Conditions: substrate (0.1 mmol), Pt/P25 (12 mg), 2-propanol (1 mL), HCl (37 wt%, 10 μL), 370 nm, room temperature, 16 h, GC yields.

Scheme S1. Photocatalytic hydrogenolysis and hydrogenation of lignin-derived aromatics on Pt/P25.
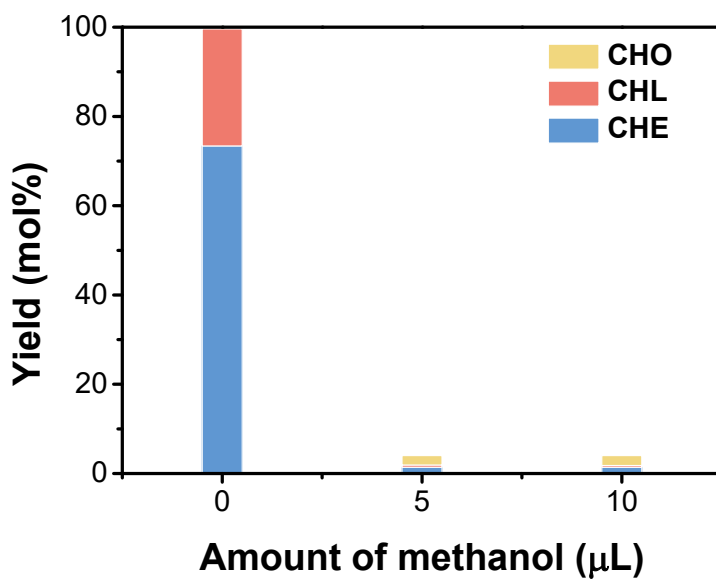
Figure S10. The effect of methanol on hydrogenation of phenol. Conditions: diphenyl ether (0.1 mmol), 4%-Pt/P25 (12 mg), HCl (1.2 equiv.), 2-PrOH (1 mL), methanol (0-10 μL) argon, room temperature, and GC yields.
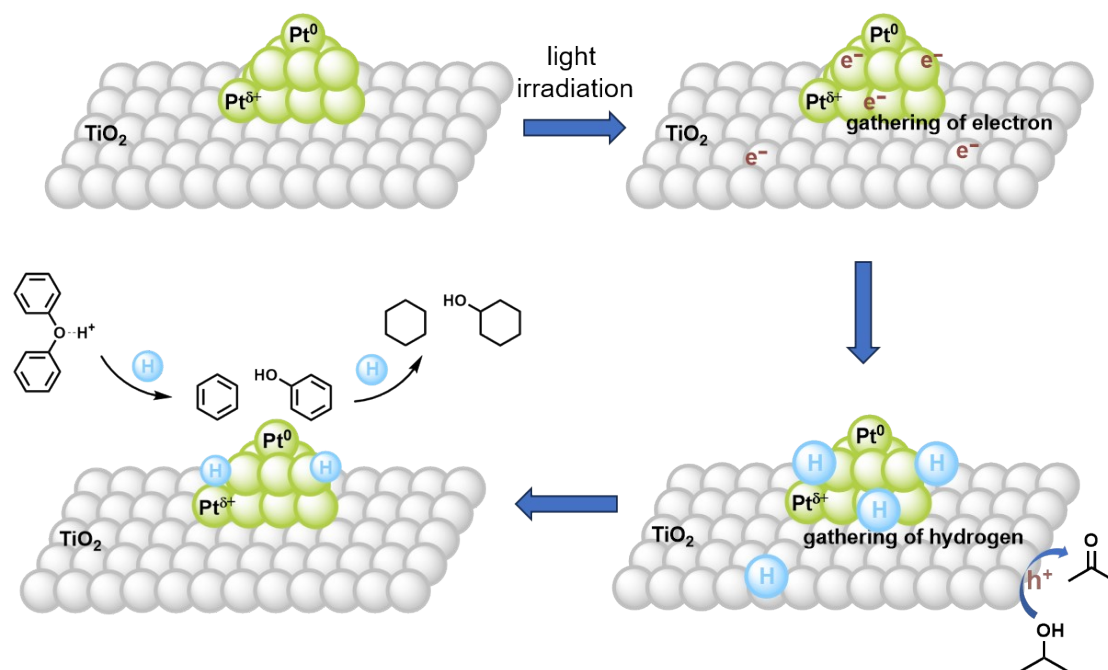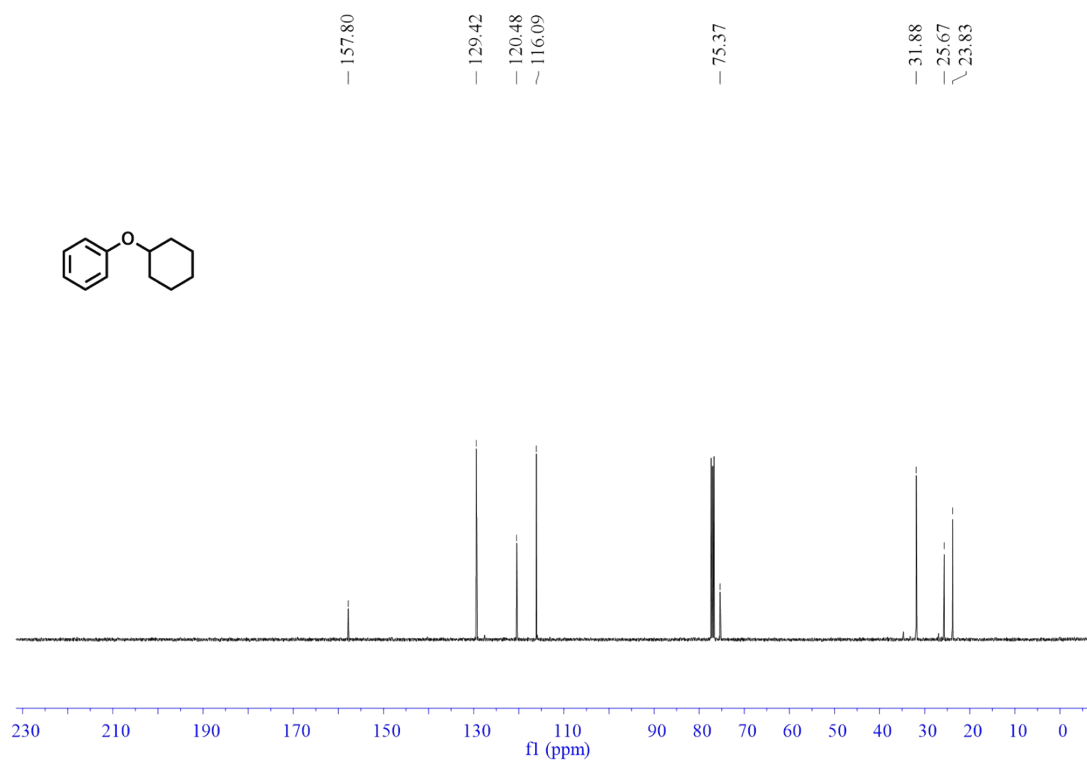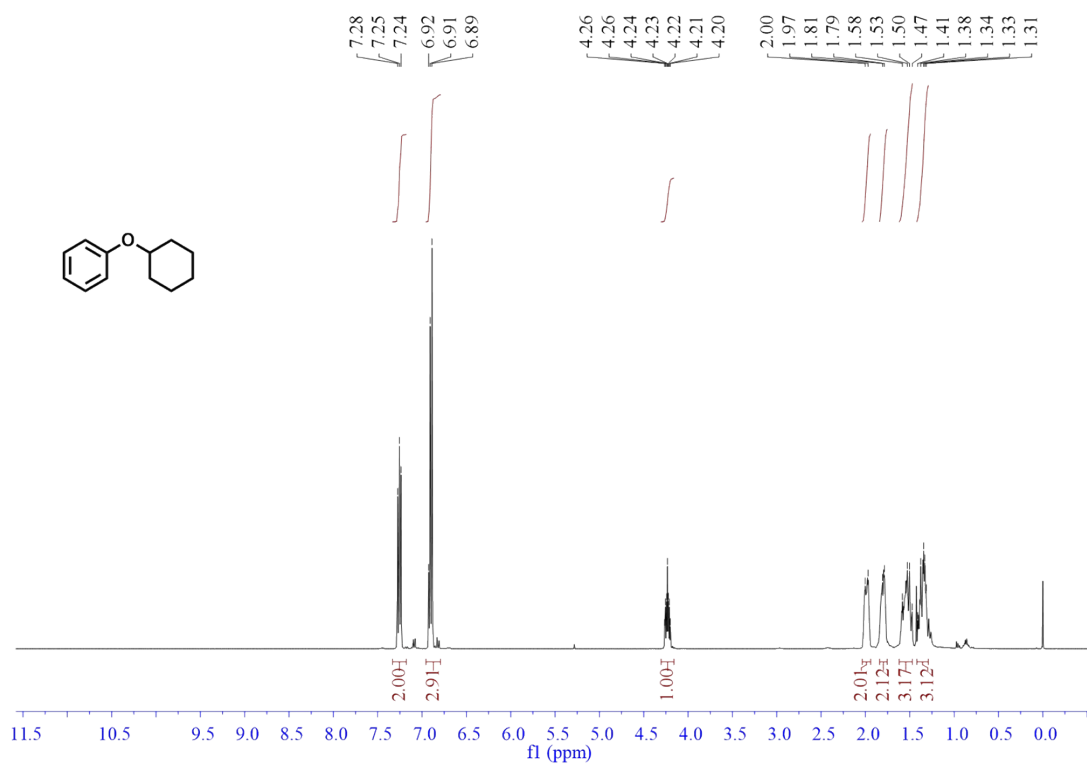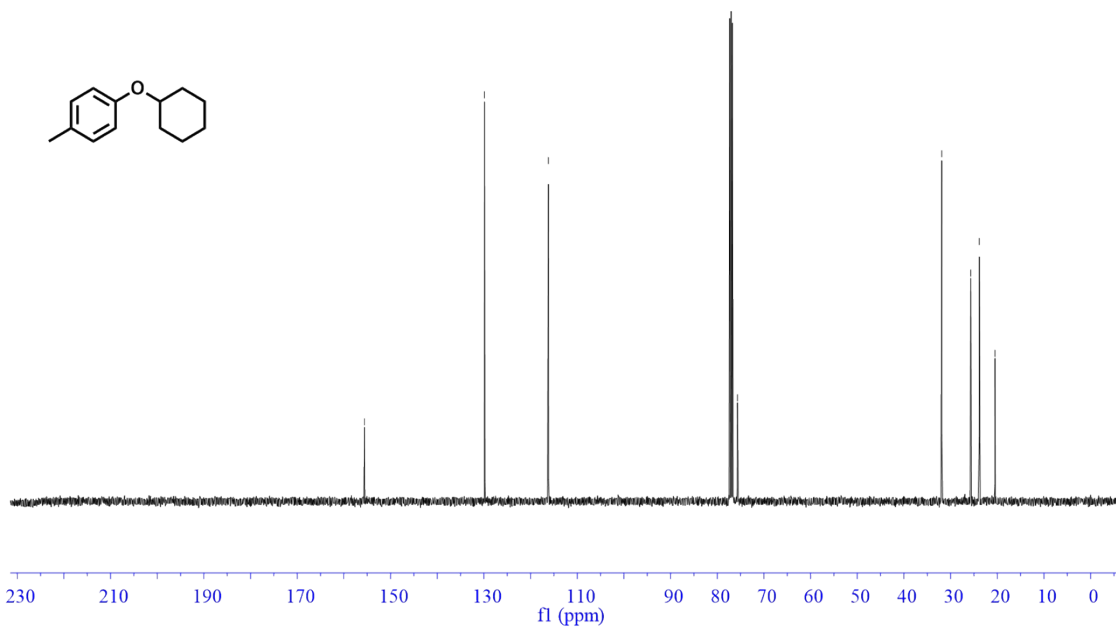

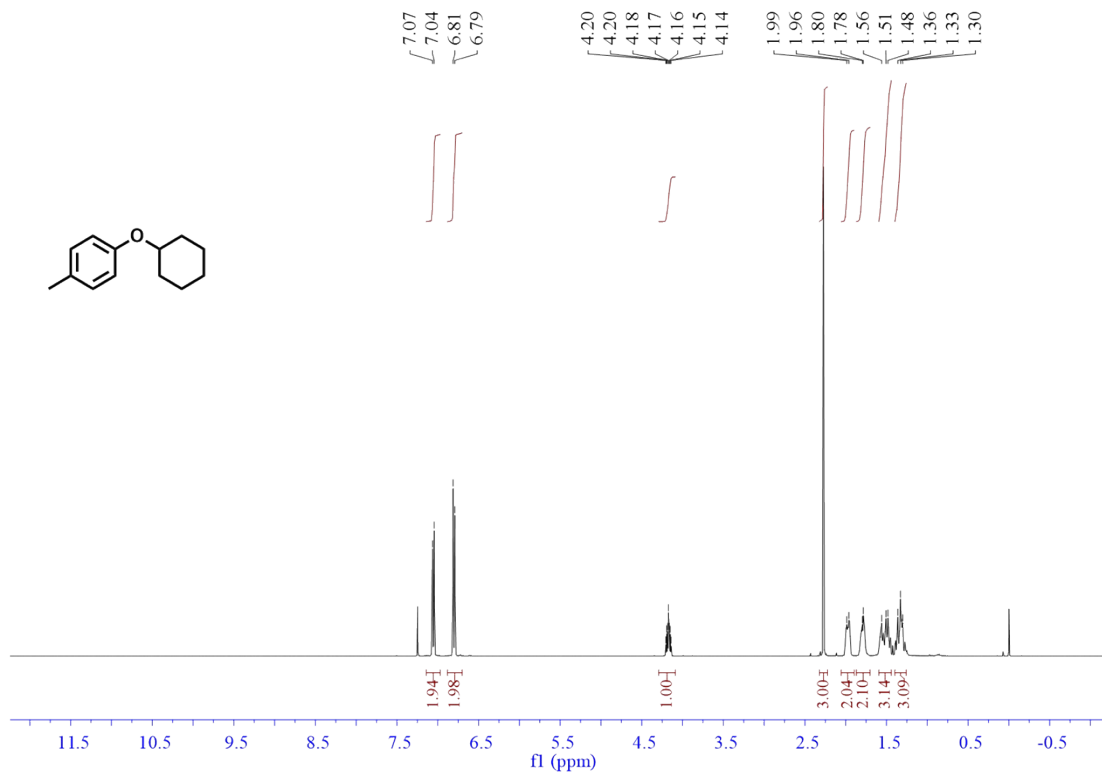**Figure S11.** The proposed mechanism of photocatalytic transfer hydrogenolysis of aryl ether.

NMR spectra of prepared substrates

^{1}H NMR and ^{13}C NMR spectra

7.07, 7.04, 6.81, 6.79
4.20, 4.20, 4.18, 4.17, 4.16, 4.15, 4.14
1.99, 1.96, 1.80, 1.78, 1.56, 1.51, 1.48, 1.36, 1.33, 1.30

1.94, 1.98, 1.00, 3.00, 2.04, 2.10, 3.14, 3.09

155.59, 129.87, 116.18, 75.66, 31.91, 25.69, 23.85, 20.49

References

[1]   a) G. Kresse, J. Furthmüller, *Comp. Mater. Sci.* **1996**, *6*, 15-50; b) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169-11186; c) G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758-1775.

[2]   J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.