Supporting Information

Photocatalytic hydrogenolysis of C–O bonds in lignin model compounds and lignin bio-oil over Ru-supported holey g-C_3N_4 exfoliated nanosheets

Himanshu Dhiman,[a] Arjun K Manal,[a] and Rajendra Srivastava[a]*

[a]Catalysis Research Laboratory, Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, Punjab-140001, India

---

*Email: rajendra@iitrpr.ac.in

*Phone: +91-1881-232064

This Supporting Information has Thirty eight pages (S1-S38), and contains:

Seven Supporting Table (Table S1-S7)

Twenty one Supporting Figures (Fig. S1-S21)

One Scheme (Scheme S1)

S1 Experimental section

Materials

Diphenyl ether, Benzyl phenyl ether, 2-phenylethyl phenyl ether, 2-phenoxy phenol, 2-phenoxy-1-phenylethanol, Melamine, Sodium borohydride, Ruthenium chloride trihydrate IPA, ACN, chemicals were purchased from Sigma-Aldrich.

S1.1 Catalyst synthesis

Synthesis of Ru/ECNHS

The Ru/ECNHS catalyst was prepared by impregnation followed by thermal reduction. In a typical procedure, 200 mg of ECNS was dispersed in 15 mL of deionized (DI) water and ultrasonicated for 30 min. The suspension was then stirred magnetically for an additional 30 min. Separately, an appropriate amount of $RuCl_3 \cdot xH_2O$ was dissolved in 5 mL of DI water and added dropwise to the ECNS suspension under continuous stirring. The resulting mixture was stirred at 500 rpm for 4 h, then heated at 65 °C to dryness. The obtained greyish-black solid was ground to a fine powder in a mortar and pestle, and reduced at 450 °C for 3 h under a H_2/Ar atmosphere in a tubular furnace. The resulting black solid was denoted as x% Ru/ECNHS, where x corresponds to the Ru loading in wt%.

Synthesis of Ru/ECNHS ($NaBH_4$ chemical reduction)

Chemically reduced Ru/ECNHS catalysts were synthesized via an impregnation–reduction approach using sodium borohydride as the reducing agent. In a typical synthesis, 200 mg of ECNS was dispersed in 15 mL of DI water and ultrasonicated for 30 min to achieve uniform suspension, followed by magnetic stirring for an additional 30 min. Separately, a calculated amount of $RuCl_3.xH_2O$ (corresponding to 2 wt%) was dissolved in 5 mL of DI water and introduced dropwise into the ECNS dispersion under continuous stirring. The resulting mixture was maintained at 500 rpm for 4 h to allow effective impregnation. Subsequently, an aqueous $NaBH_4$ solution (100 mg in 10 mL) was added dropwise to ensure complete reduction of Ru species. The reaction mixture was then stirred overnight (12 h). The solid product was recovered by centrifugation at 11,000 rpm for 4 min per cycle, washed, and dried in an oven at 60 °C for 12 h. The obtained black solid was finely ground using a mortar and pestle to yield chemically reduced 2 wt% Ru/ECNHS.

Synthesis of metal-decorated catalysts

The Cu, Ni, Pd, and Ag-loaded catalysts were prepared via a wet impregnation method followed by thermal reduction. In a typical synthesis, 200 mg of ECNS was dispersed in 15 mL of DI water and ultrasonicated for 30 min, followed by magnetic stirring for an additional 30 min. Separately, an appropriate amount of the corresponding metal precursor—$Cu(NO_3)_2{\cdot}3H_2O$ for Cu (weight corresponding to 2wt% or 5 wt%), $Ni(NO_3)_2{\cdot}6H_2O$ for Ni (weight corresponding to 2wt% or 5 wt%), $AgNO_3$ for Ag (weight corresponding to 2 wt%), and $PdCl_2.H_2O$ for Pd (weight corresponding to 2 wt%) was dissolved in 5 mL of deionized water and added dropwise to the ECNS suspension under continuous stirring. The resulting mixtures were stirred at 500 rpm for 4 h and then heated at 65 °C until dryness. The obtained solids were ground into fine powders and subsequently reduced at 450 °C for 3 h under a H_2/Ar atmosphere in a tubular furnace to yield 5% Cu/ECNHS, 5% Ni/ECNHS, 2% Ag/ECNHS, and 2% Pd/ECNHS, respectively.

S1.2. Catalytic reaction procedure

Photocatalytic reaction conditions for lignin bio-oil and native lignin

Photocatalytic reactions were conducted in a home-made glass reactor, irradiated with a blue LED, fitted with a cooling fan for the desired reaction period. The photograph of the photocatalytic setup and the light absorption characteristics of the blue LED are provided in the SI (Fig. S1). For lignin bio-oil, identical catalyst loading (10 mg of 2% Ru/ECNHS) and substrate amount (0.1 mmol) were employed. In the case of native lignin, due to its polymeric and recalcitrant nature, slightly modified reaction conditions were applied. Specifically, 100 mg of native lignin and 30 mg of 2%Ru/ECNHS were used, with a reaction time of 24 h. Additionally, a small amount of HCl (40 µL) was introduced to facilitate substrate activation. Apart from these necessary adjustments, the overall reaction system—including the light source, solvent, and H_2 pressure—remained consistent with that used for the model compound studies.

Quantification of Acetone Formed during the Photocatalytic Reaction

$$\text{The amount of IPA taken in reaction mixture } = \boldsymbol{x}\ mL$$

$$\text{The yield of acetone formed during the 1 h of photoreaction of VAN} = y\ \%$$

$$\text{The amount of acetone formed after photoreaction of VAN} = \mathbf{x} \times \frac{\boldsymbol{y}}{100} = \boldsymbol{z}\ mL$$

$$Density\ of\ acetone\ (d) = 0.784\ g\ mL^{-1} = \frac{\text{Mass } (m)}{\text{Volume } (V)}$$

$$Mass\ of\ acetone\ (m) = d \times V = 0.784\ g\ mL^{-1}\ \times \boldsymbol{z}\ mL = \mathbf{a}\ g$$

$$Moles\ of\ acetone\ formed\ during\ \text{photoreaction of VAN} = Mass\ of\ acetone\ \times \frac{1\ mole}{58.08\ g}$$

$$Moles\ of\ acetone\ formed\ during\ \text{photoreaction of VAN} = \boldsymbol{a}\ g\ \times \frac{1\ mole}{58.08\ g} = \boldsymbol{b\ mmoles} = \boldsymbol{b}\ \mathbf{x\ 1000}\ \boldsymbol{\mu}\mathbf{moles}$$

Catalyst characterisation

Tauc plot for band gap calculations

The equation ($(\alpha h\nu)^{1/r} = \beta(h\nu - E_g)$) was utilised to determine the band gap. The value of r is contingent on the transition nature, where r = ½ is appropriate for direct and r = 2 signify indirect transitions. The $(\alpha h\nu)^{1/r}$ vs. (hν) plots with r = ½, enabling estimation of the band-gap for direct allowed transitions by straight line extrapolation in the case of g-C_3N_4.[S1]

Time-Correlated Single Photon Counting

The data analysis employed double-exponential fitting to determine the average lifetimes and their percentage contributions, employing the equation ($y = y_{\circ} + \sum_{i=1}^{n} \alpha_i e^{-(\frac{t}{\tau_i})}$). To calculate the average decay time, ⟨τ⟩, the $\langle\tau\rangle = \frac{\sum_{i=1}^{n} \alpha_i \tau_i^2}{\sum_{i=1}^{n} \alpha_i \tau_i}$ was utilised, and $\sum \alpha_i$ was normalised to 1.[S2]

Mott-Schottky analysis

This method involved the relation $1/C^2 = 2[V\text{-}V_{fb}\text{-}(k_bT/e)]/\varepsilon\varepsilon_0 eA2N_d$).[S3] Plots of $1/C^2$ vs. applied potential were constructed. All the materials possess a positive slope, indicating their n-type semiconducting behaviour. The MS plots x-intercepts yielded the flat-band position (E_{fb}), which was -1.27 V vs. Ag/AgCl for g-C_3N_4 (Fig. S12). In n-type semiconductors, the E_{fb}

lies below to conduction band (CB) edge.[S1] The E_{fb} values were used to determine the position of the CB edge (E_{CB}) through the relation $E_{CB} = E_{fb}$ -0.1 V. Potential values were standardized using the equation ($E_{NHE} = E_{Ag/AgCl} + 0.196$), and Tables S3 & S5 presents the calculated E_{CB} vs. NHE values for all the material.[S4] Finally, the valence band positions (E_{VB}) were obtained by applying the relation $E_{VB} = E_{CB} + E_g$, where E_{CB} represents the conduction band potential and E_g is the band gap.

Photoelectrochemical measurement

The photoelectrochemical analyses were performed with PGSTAT302N Autolab electrochemical workstation using standard three-electrode grouping in Pyrex cell with a 0.1 M aqueous sodium sulfate solution as electrolyte. The coated photocatalyst acts as a photoanode (working electrode), Pt wire electrode as a counter electrode, and Ag/AgCl as a reference electrode. Photoanode was prepared by coating photocatalyst on glass slides containing fluorine-doped tin oxide (FTO), cleaned with acetone, rinsed with DI water, and oven-dried before use. The catalyst was coated over the FTO surface using the drop-casting method. To make a binder solution, 1.5 ml of ethanol was mixed with 1 ml of water and 40 µl of nafion. 20 mg of the photocatalyst was added in the binder solution and sonicated for 10 minutes. The binder solution was cast dropwise over the glass surface using a dropper and hotplate with a temperature of 45 °C. The electrochemical impedance spectroscopy was calculated in the frequency range of 1 MHz to 1 Hz using a sinusoidal AC perturbation signal of 5 mV. The mott-schottky experiment was conducted at 1000 Hz constant frequency in dark conditions. LSV and transient photocurrent measurements were carried out under dark and illumination conditions using a 300 W Xenon arc lamp (Newport-R22) with a cut-off filter ($\lambda >$ 420 nm and intensity of 100 $mW.cm^{-2}$).

Materials characterisation

Physicochemical characterisation

X-ray diffraction (XRD) patterns were collected using a RIGAKU Mini-flex diffractometer with Cu Kα radiation over the 2θ range of 5° to 80°. Surface area and porosity were determined via N_2 adsorption-desorption measurements using the BELSORP instrument. Prior to N_2 adsorption, all materials were degassed at 200 ˚C for 4 h in the degassing port. The specific surface area was calculated by applying the Brunauer-Emmett-Teller (BET) equation to the relative pressure range of 0.05 to 0.3. The FESEM analysis of the material's morphology was carried out using a Joel instrument at an accelerating voltage of 10 kV. UV-DRS study of all catalysts was performed on a Shimadzu UV-visible spectrophotometer (UV-2600) using $BaSO_4$ as standard reference material. X-Ray photoelectron spectroscopy (XPS) was carried out using a Thermofisher scientific 'ESCALAB Xi+' instrument. UPS and VBXPS analyses were performed using the same instrument. Fluorescence analysis was conducted using a Perkin Elmer LS55. Finally, fluorescence decay time was evaluated using the TCSPC instrument of DeltaFlex TCSPC Lifetime Fluorimeter at IRCC IIT Bombay. Fourier transform infrared (FT-IR) analysis was conducted using the Bruker Tensor-II instrument. Transmission electron microscopy (TEM) analysis was obtained for an in-depth study of material on (FEI THEMIS 300 kV) instrument operating at 300 kV.

Reaction procedure

Analysis of the reaction mixture

To evaluate the composition and selectivity of the products, GC analysis was performed using a Shimadzu 2010 GC system equipped with a RXi-5Sil MS column (30 m x 0.25 mm x 0.25 µm). The carrier gas was high-purity nitrogen (99.99% GC grade) with a flow rate of 10 ml/min, and hydrogen (99.99% GC grade) and air (99.99% GC grade) were used as the ignition gases. The injector and detector temperatures were set at 280 °C. The GC column oven temperature was programmed as follows: initial temperature of 80 °C with a hold time of 2 minutes, followed by a ramp to a final temperature of 280 °C with a ramp rate of 5 °C/min. A 0.2 µL sample was injected for analysis. In the DPE transformation, the resulting chromatogram showed the presence of five compounds diphenyl ether (DPE), benzyl cyclohexyl ether (BCE), dicyclohexyl ether (DCE), Phenol (Phe), cyclohexanol (CyOH) and cyclohexane (CH). The products were confirmed using GC-MS with a Shimadzu GCMS-QP 2010 Ultra instrument equipped with an Rtx-5 Sil MS column (30 m x 0.25 mm x 0.25 µm).

GC calibrations for relative selectivity of products

The calibration curves for DPE, PPE, BPE and their reduced products (CyOH, CH, Phe, TOL, EB) were constructed by employing various concentrations of the analytes. The substrate conversion also calculated by considering the remaining GC area of the substrate in the sample, the GC area of dodecane in the sample, and the initial weight of the loaded substrate before the reaction. The yield of products was calculated by assessing the area of the of the product in the sample relative to the area of dodecane in the GC chromatogram. The detailed calculation was as follows:

$$dodecane\ (mmol) = \frac{Weight\ of\ dodecane\ in\ sample}{\text{MW of dodecane}} \text{……….. (S1)}$$

$$CProduct\ (mmol) = \frac{GC\ peak\ area\ ofproduct\ in\ sample}{\text{GC peak area of dodecane in sample}} \ldots\ldots\ldots.\text{(S2)}$$

$$Mass\ of\ product = mmol\ of\ product \text{ x MW of product……….(S3)}$$

$$Conversion\ = \frac{\text{(Initial area \% of Substrate} - \text{Final area \% of Substrate)}}{\text{Initial area \% Substrate}} \text{ x 100} \ldots\ldots\ldots.\text{(S4)}$$

$$Selectivity\ (\%) = \frac{(Peak\ area\ ofproduct\ in\ sample)}{(Peak\ area\ oftotal\ products\ in\ sample} \text{ x 100} \ldots\ldots\ldots.\text{(S5)}$$

$$Conversion\ of\ lignin\ (\%) = \frac{\text{(Initial weight fo lignin} - \text{Final weight fo lignin)}}{\text{Initial weight fo lignin}} \text{ x 100..(S4)}$$

$$Yield\ of\ lignin\ bio - oil\ (\%) = \frac{\text{(Weight of lignin bio} - \text{oil otabined from lignin)}}{\text{Weight of lignin taken}} \text{ x 100..(S4)}$$

The response factor was calculated using the following expression:

$$\frac{Area_{\ Analyte}}{[Analyte]} = F\ \frac{Area_{\ Internal\ standard}}{[Internal\ standard]} \text{…….. (S6)}$$

Where, F is the response factor, $\text{Area}_{\text{Analyte,}}$ and $\text{Area}_{\text{Internal standard}}$ are areas under the peaks of Analyte and, Internal standard respectively. [Analyte] and [Internal standard] are concentrations of Analyte and Internal standard, respectively.

Apparent Quantum Yield Calculation

The quantum yield of the reaction was calculated using eq (S4), which gives the ratio between the electron involved in the reaction and the molar flow of photons introduced into the reactor. The apparent wavelength (λ) of photons was estimated from the band gap of the catalyst, determined from Tauc plots. The quantum yield calculated in this manner was not the exact value but served as a reference to compare the photo efficiency of the photocatalytic system.

$$Apparent\ Quantum\ Yield\ (\phi)\ = \frac{Number\ of\ reacted\ electron \times 100}{Number\ of\ incident\ photon} \qquad \text{(S1)}$$

$$Number\ of\ reacted\ electron = Reactant\ conversion\ (mol^{-1})\ \times\ N_A\ (mol) \qquad \text{(S2)}$$

$$Number\ of\ incident\ photon = \frac{Light\ intensity\ (Wm^{-2}) \times Area\ (m^2) \times Time\ (s)}{\frac{h\ (Js)\ c\ (ms^{-1})}{\lambda\ (m)}} \qquad \text{(S3)}$$

$$\phi = \frac{Reactant\ conversion\ (mol) \times N_A(mol^{-1}) \times h\ (Js) c\ (ms^{-1})}{Light\ intensity\ (Js^{-1}m^{-2}) \times Area\ (m^2) \times Time\ (s) \times \lambda\ (m)} \qquad \text{(S4)}$$

TOF Calculation

$$TOF = \frac{Moles\ of\ reactant\ consumed}{Moles\ of\ active\ metal\ X\ time\ (h)} \qquad \text{(S5)}$$

Dispersion % of Ru from TEM analysis

The % dispersion with the help of TEM images was calculated as follows

$$\text{Dispersion (\%)} = \frac{1\ \text{nm}}{avg\ d(nm)} \times 100 \qquad \text{(S6).}$$

Calculation of Sustainable Green Metrics

- $\boldsymbol{Atom\ Economy}\ (\%) = \frac{\boldsymbol{Molar\ mass\ of\ the\ desired\ products}}{\boldsymbol{Molar\ mass\ of\ reactants}} \times \mathbf{100}$

  Atom economy (%) was determined by dividing the combined molar masses of the desired products (CyOH and CH) by the total molar masses of the reactants (DPE and H_2), and multiplying the resulting ratio by 100.

- $\boldsymbol{Reaction\ Mass\ Efficiency}\ (\%) = \frac{\boldsymbol{Produced\ mass\ of\ the\ desired\ products}}{\boldsymbol{Utilized\ mass\ of\ reactants}} \times \mathbf{100}$

  Reaction Mass Efficiency (%) is determined by dividing the total mass of products obtained (g) by the total mass of reactants consumed (g), followed by multiplication by 100.

- $\boldsymbol{Atom\ Efficiency}\ (\%) = \frac{\boldsymbol{Atom\ Economy}\ (\%) \times \boldsymbol{Yield}\ (\%)\ \boldsymbol{of\ the\ desired\ products}}{\mathbf{100}}$

Atom Efficiency (%) is determined by multiplying the Atom Economy (%) by the Yield (%) of the desired products and dividing the result by 100.

- $\boldsymbol{E - factor \ = \frac{mass\ of\ waste\ generated}{mass\ of\ desired\ products}}$

  The E-factor is calculated by dividing the mass of waste generated by the mass of desired products (CyOH and CH). In this calculation, 90% solvent (IPA) recovery is assumed, with 10% accounted as loss during product isolation.

- $\boldsymbol{Process\ Mass\ Intensity = \frac{Total\ mass\ of\ all\ materials\ used\ in\ process}{Mass\ of\ desired\ products}}$

  Process mass intensity is calculated by dividing the total mass of all materials used in the process (reactants, solvent, and catalyst) (g) by the mass of desired products (g). In this assessment, a 90% solvent recovery during product extraction is also assumed.

- $\boldsymbol{Energy\ economy\ co - efficient\ \ (\varepsilon) = \frac{Yield\ (\%)\ of\ desired\ products}{Lamp\ power\ (W) \times Time\ (min)}}$

  Energy economy co-efficient (ε) is calculated by taking the ratio of Yield (%) of desired products with the product of Lamp power (W) and Time (min).

- $\boldsymbol{Environment\ Energy\ Impact\ Factor\ (\xi\ ) = \frac{E{-}factor}{Energy\ economy\ co{-}efficient\ (\varepsilon)}}$

  Environment Energy Impact Factor (ξ) is calculated by taking the ratio of E-factor and Energy economy co-efficient (ε).

Table S1 The textural properties of catalysts prepared in this study.

Entry	**Catalyst**	**BET surface area (m^2g^{-1})**	**Total pore volume ($cm^3\ g^{-1}$)**
1	BCN	17.4	0.079
2	ECNS	26.7	0.119
3	Ru/ECNHS	48.5	0.175
4[a]	Ru/ECNS-($NaBH_4$)	12.1	0.061

Surface area calculated by BET equation. Total pore volume was determined using the t-plot method. [a]Catalyst prepared using $NaBH_4$ as a reducing agent.

Table S2 Comparative catalytic activities with the reported literature.

S.No.	**Catalyst**	**Reaction conditions**	**Light source**	**DPE Conv. (%)**	**CyOH Sel. (S) (%)/ Yield (Y) (mol %)**	**CH Sel (%)/ Yield (Y) (mol %)**	**TOF (h^{-1})**	**Reference**
1.	5% Pd@CN/ rGO/BMO(2:1)	DPE (0.1 mmol), photocatalyst (20 mg), IPA (5 mL), H_2 (5 bar), 24 h.	150 W white LED	74.6	4.6(S)	93.4 (S)	0.33 h^{-1}	S5
2.	4.4% Pt@CDs/TiO_2-MP	DPE (0.025 mmol), 12 mg photocatalyst , IPA (1 mL), N_2 , 10 h.	300 W xenon 365 nm visible light	87.8	48.3 (S)	36.1 (S)	0.81 h^{-1}	S6
3.	4%-Pt/P25	DPE (0.1 mmol), 12 mg photocatalyst, IPA (1 mL), 1.2 eq. HCl, Ar, 16 h.	18 W LED (365 nm)	99.0	25.0 (Y)	73.0 (Y)	2.51 h^{-1}	S7
4.	2% Ru/ECNHS	DPE (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 6 h.	15 W blue LED	99.9	90.0 (Y)	92.8 (Y)	8.40 h^{-1}	This work

Table S3 Photocatalytic hydrogenolysis of lignin model compounds.

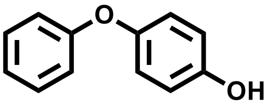
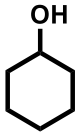
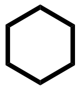
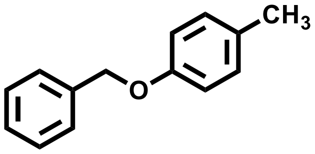
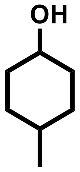
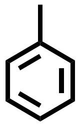
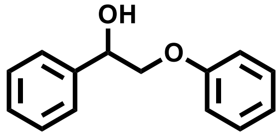
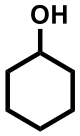
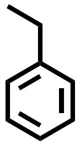
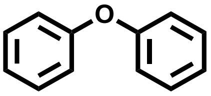
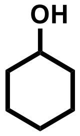
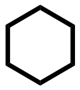
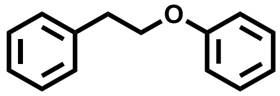
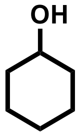
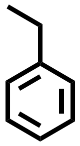
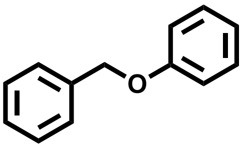
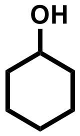
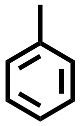
S.No.	**Substrate**	**Condition**	**Conv. (%)**	**P-1 (Yield (mol %))**	**P-2 (Yield (mol %))**
1.		Substrate (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 12 h.	~99	 176%	 8.9%
2.		Substrate (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 12 h.	~99	 89.6%	 93.2%
3.		Substrate (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 12 h.	~99	 93.7%	 95.3%
4.		Substrate (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 12 h.	~99	 95.2%	 96.8%
5.		Substrate (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 12 h.	~99	 97.1%	 98.4%
6.		Substrate (0.1 mmol), 10 mg photocatalyst, IPA (5 mL), H_2 (4 bar), 12 h.	~99	 97.6%	 98.5%

Table S4 Reaction of simulated bio-oil with Ru/ECNHS.

S.No.	**Time**	**Conversion (%)**	**CyOH Yield (mol %)**	**CH Yield (mol %)**	**Tol Yield (mol %)**	**EB Yield (mol %)**	**Phe Yield (mol %)**
1.	3	DPE (51.0 %) PPE (63.0 %) BPE (85.0 %)	24.4	23.3	53.8	55.4	28.1
2.	9	DPE (98.0 %) BPE (99.9 %) PPE (99.0 %)	86.2	90.1	93	92.1	5.0

CyOH = cyclohexanol; CH = cyclohexane; Tol = toluene; EB = ethyl benzene; Phe = Phenol

Table S5. Hydrogenation of lignin bio-oil with 2% Ru/ECNHS.

Lignin mass	**Condition**	**Bio-oil yield (wt %)**	**Selectivity guaiacyl (G) units (%)**	**Selectivity of syringyl (S) units (%)**
100 mg	10 mg 2% Ru/ECNHS, IPA (5 mL), H_2 (4 bar), 12 h.	82 %	70.1	20.5

Table S6 The band edge potentials and bandgap of all the photocatalysts according to Mott Schottky analysis.

Entry	**Catalyst**	**Band Gap**	**Flat Band Potential vs. Ag/AgCl**	**Conduction Band edge Potential vs. Ag/AgCl**	**Conduction Band Edge Potential vs. NHE**	**Valence Band Edge Potential vs. NHE**
1	BCN	2.67	-1.27	-1.37	-1.17	1.50
2	ECNS	2.76	-1.35	-1.45	-1.25	1.51
3	Ru/ECNHS	2.90	-1.48	-1.58	-1.38	1.52

Table S7 Best fitted parameters of multiexponential components for decay curve.

Entry	**Catalyst**	**Pre-exponential functions**			**Decay Lifetime (ns)**			
		α_1	α_2	α_3	τ_1	τ_2	τ_3	$<\tau>$
1	BCN	28.3	65.7	6.0	0.92	3.29	0.27	1.38
2	ECNS	36.9	57.4	5.7	1.51	4.80	0.40	1.97
3	Ru/ECNHS	29.6	70.4	-	1.00	3.90	-	2.10

Table S8 Comparison of band gap and band edge potential values obtained from Mott Schottky analysis and UPS.

Entry	**Catalyst**	**Mott-schottky analysis**		**VB-XPS, UPS analysis**	
		Conduction Band Edge Potential vs. NHE	**Valence Band Edge Potential vs. NHE**	**Conduction Band Edge Potential vs. NHE**	**Valence Band Edge Potential vs. NHE**
1	BCN	-1.17	1.50	-1.20	1.47
2	ECNS	-1.25	1.51	-1.27	1.49
3	Ru/ECNHS	-1.38	1.52	-1.40	1.70

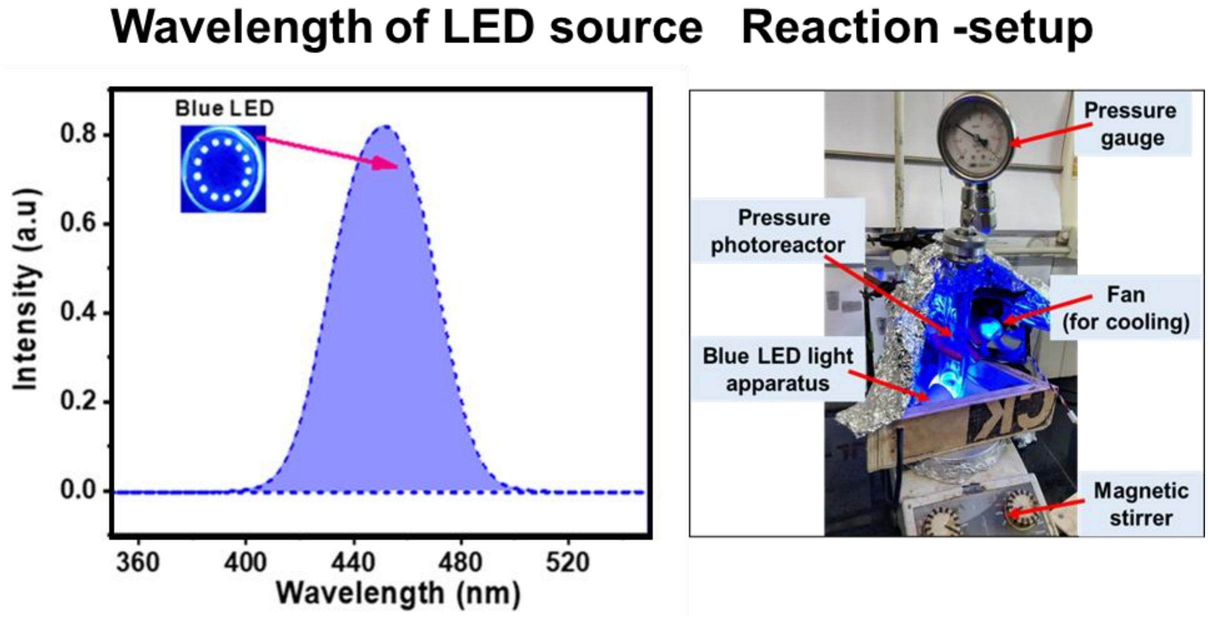


Fig. S1 Left: Wavelength characteristics of blue LED, Right: Homemade glass reactor.

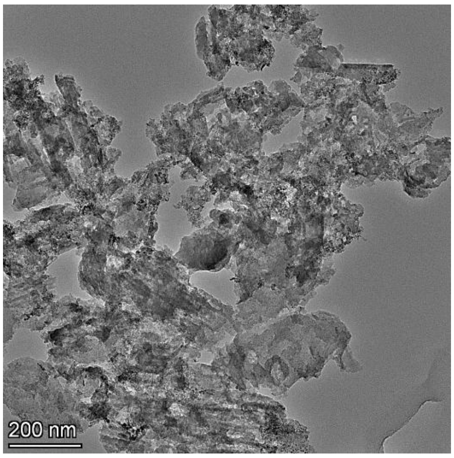


Fig. S2 TEM image of 2% Ru/ECNHS showing exfoliated nanosheet morphology.

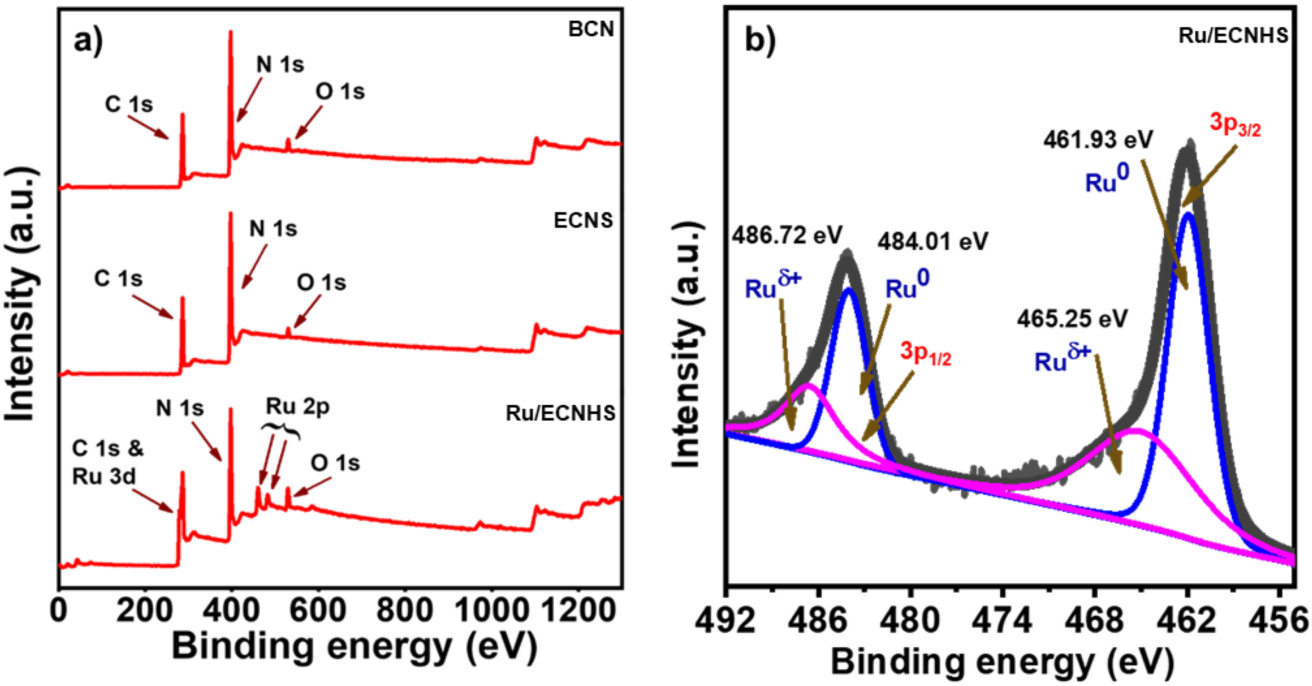


Fig. S3 a) XPS survey spectra of BCN, ECNS, Ru/ECNHS, b) Ru 3p XPS spectra of Ru/ECNHS.

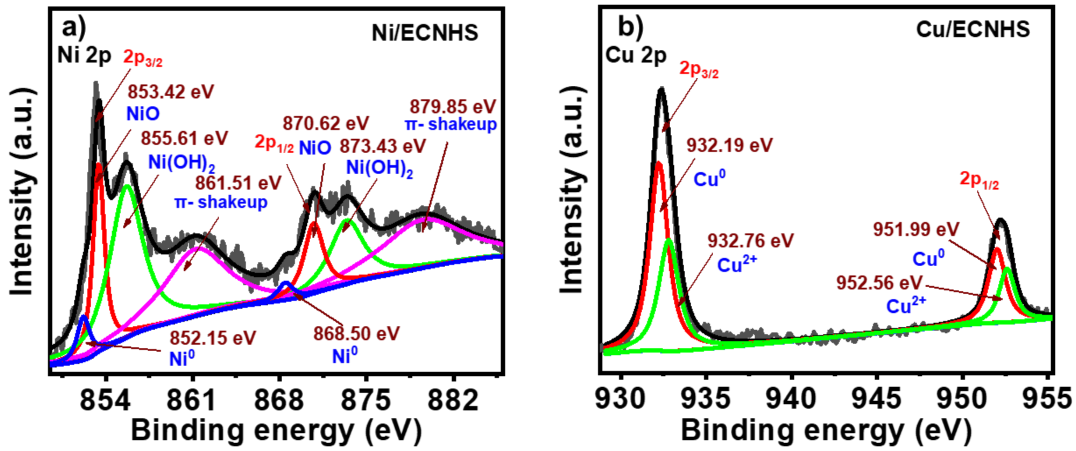


Fig. S4 High resolution XPS spectra of (a) Ni 2P, and (b) Cu 2P.

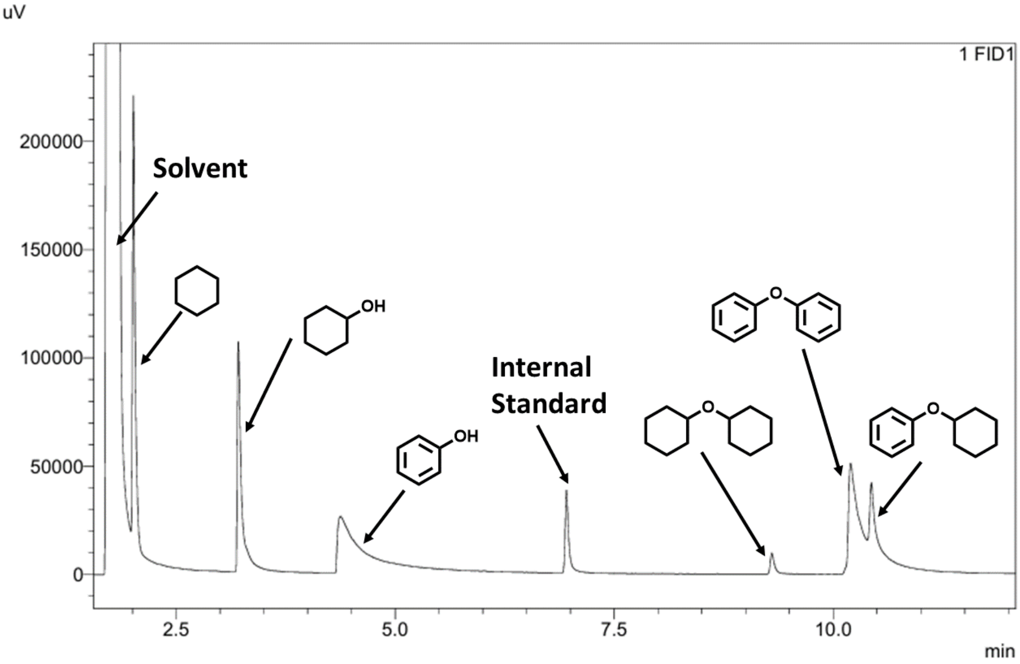


Fig. S5 GC chromatograph of obtained reaction mixture of DPE. Reaction conditions: DPE (0.1 mmol), 2%Ru/ECNHS (10 mg), IPA (5 mL), H_2 (4 bar), time (3 h), 15 W blue LED.

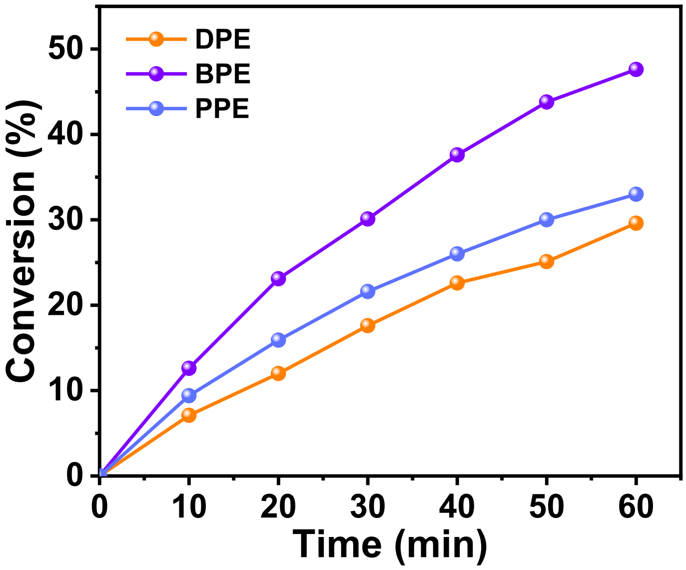


Fig. S6 Reactivity trends of DPE, BPE, PPE evaluated in initial 1 h.

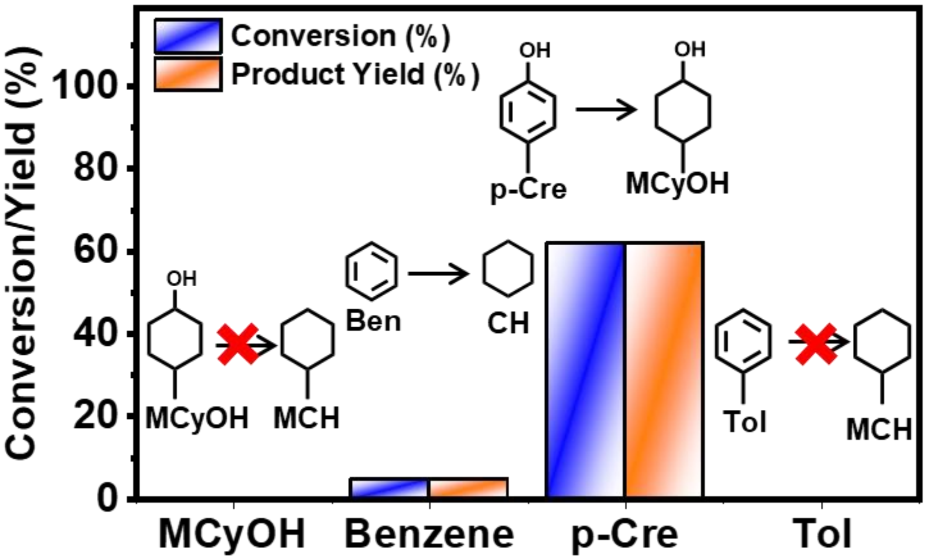


Fig. S7 Control reactions with methylcyclohexanol (MCyOH), Benzene (Ben), p-cresol (p-Cre) and Toluene (Tol). Reaction conditions: Substrate (0.1 mmol), 2% Ru/ECNHS (10 mg), H_2 (4 bar), IPA (5 mL), Time (2 h), 15 W blue LED.

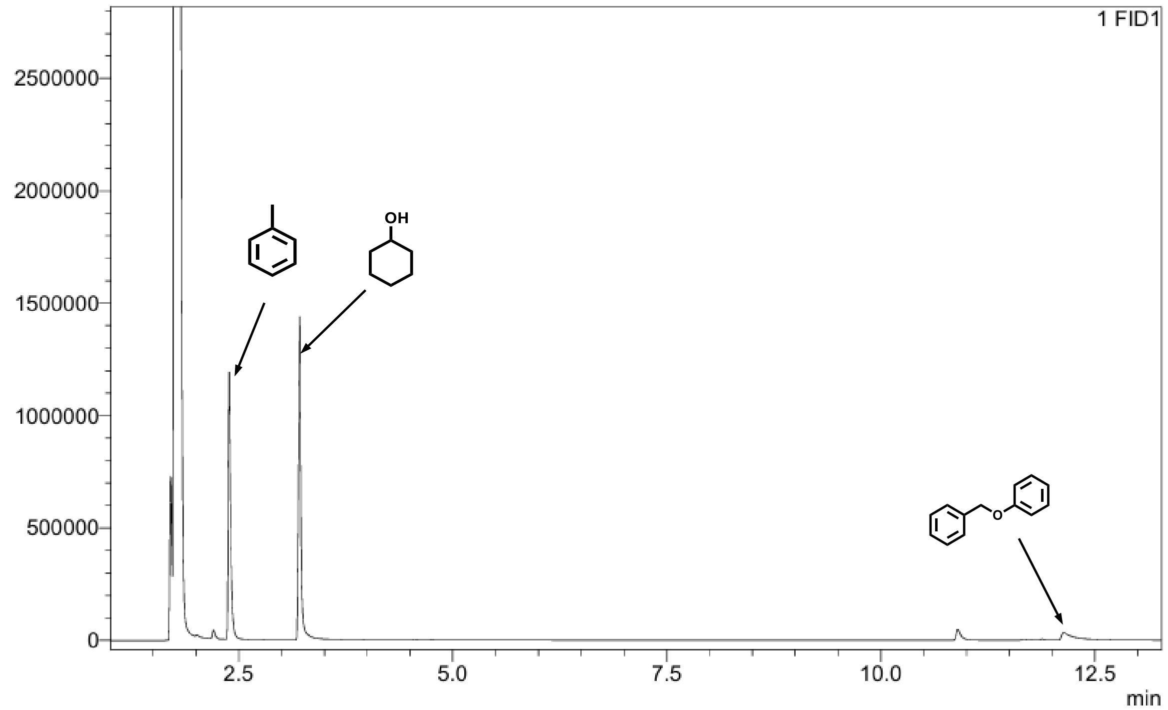
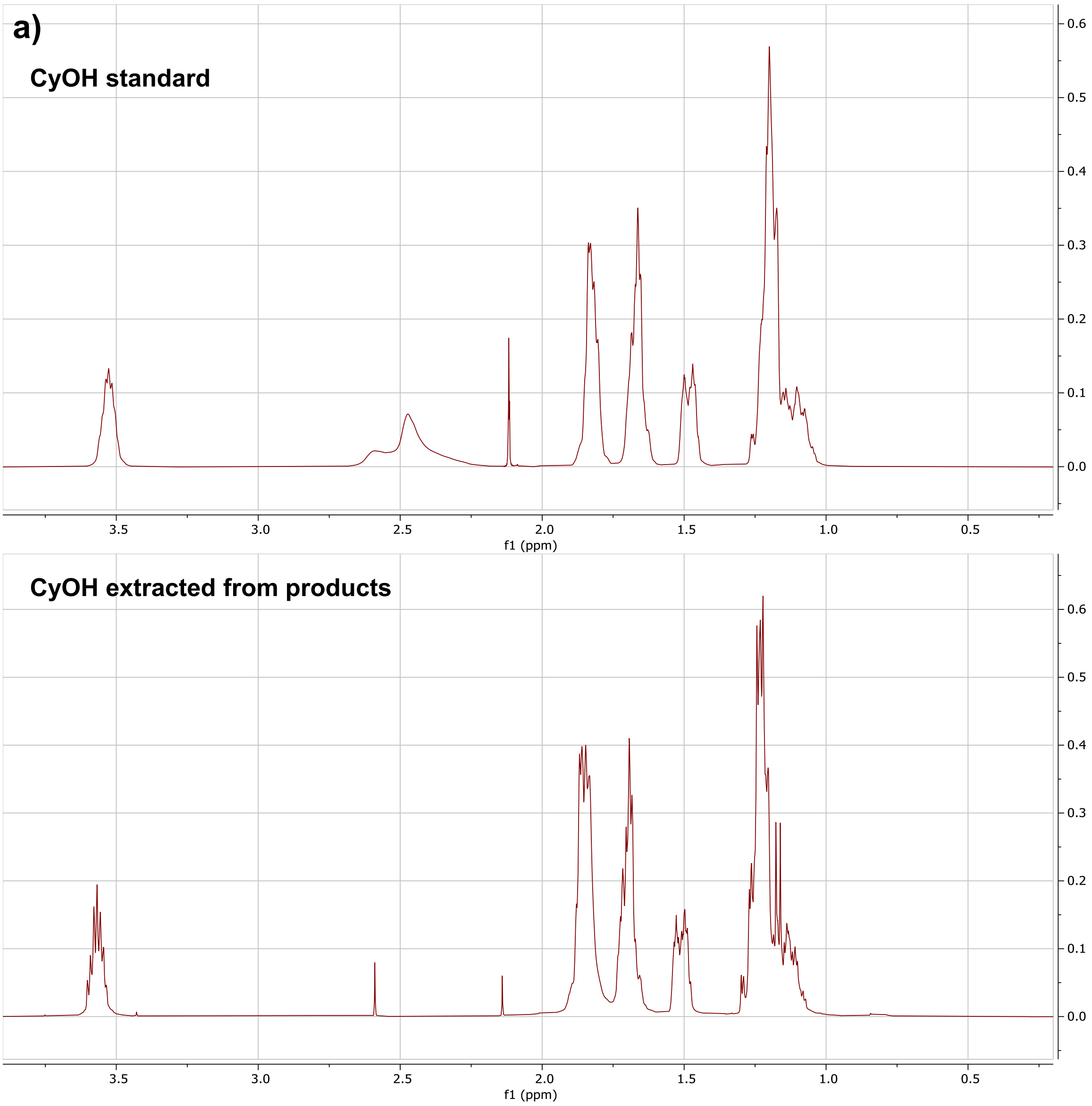
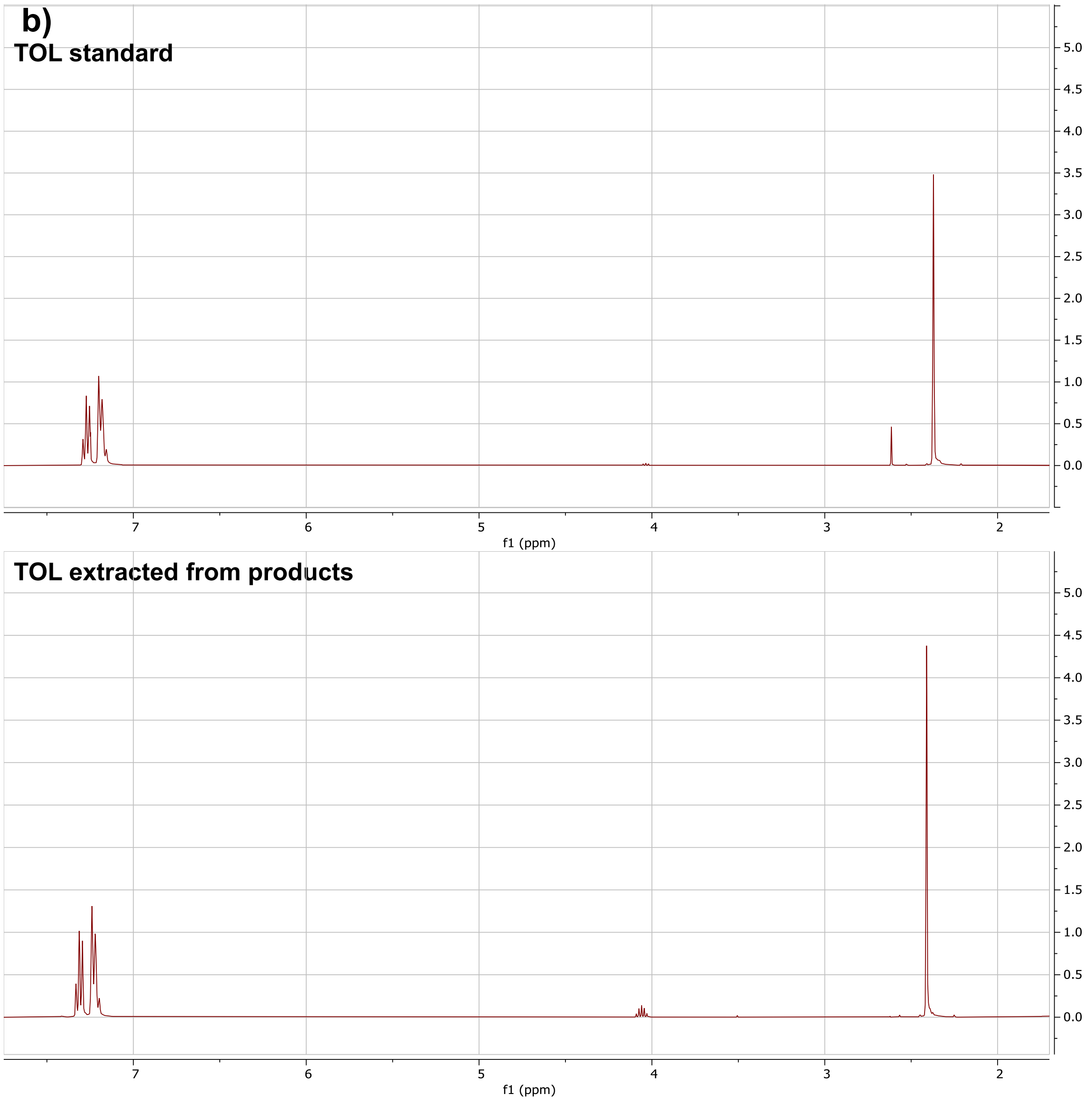


Fig. S8 GC chromatograph of obtained reaction mixture of BPE. Reaction conditions: BPE (0.1 mmol), 2%Ru/ECNHS (10 mg), IPA (5 mL), H_2 (4 bar), time (3 h), 15 W blue LED.


a)
CyOH standard
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
CyOH extracted from products
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


b)
TOL standard
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
7
6
5
4
3
2
f1 (ppm)
TOL extracted from products
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
7
6
5
4
3
2
f1 (ppm)

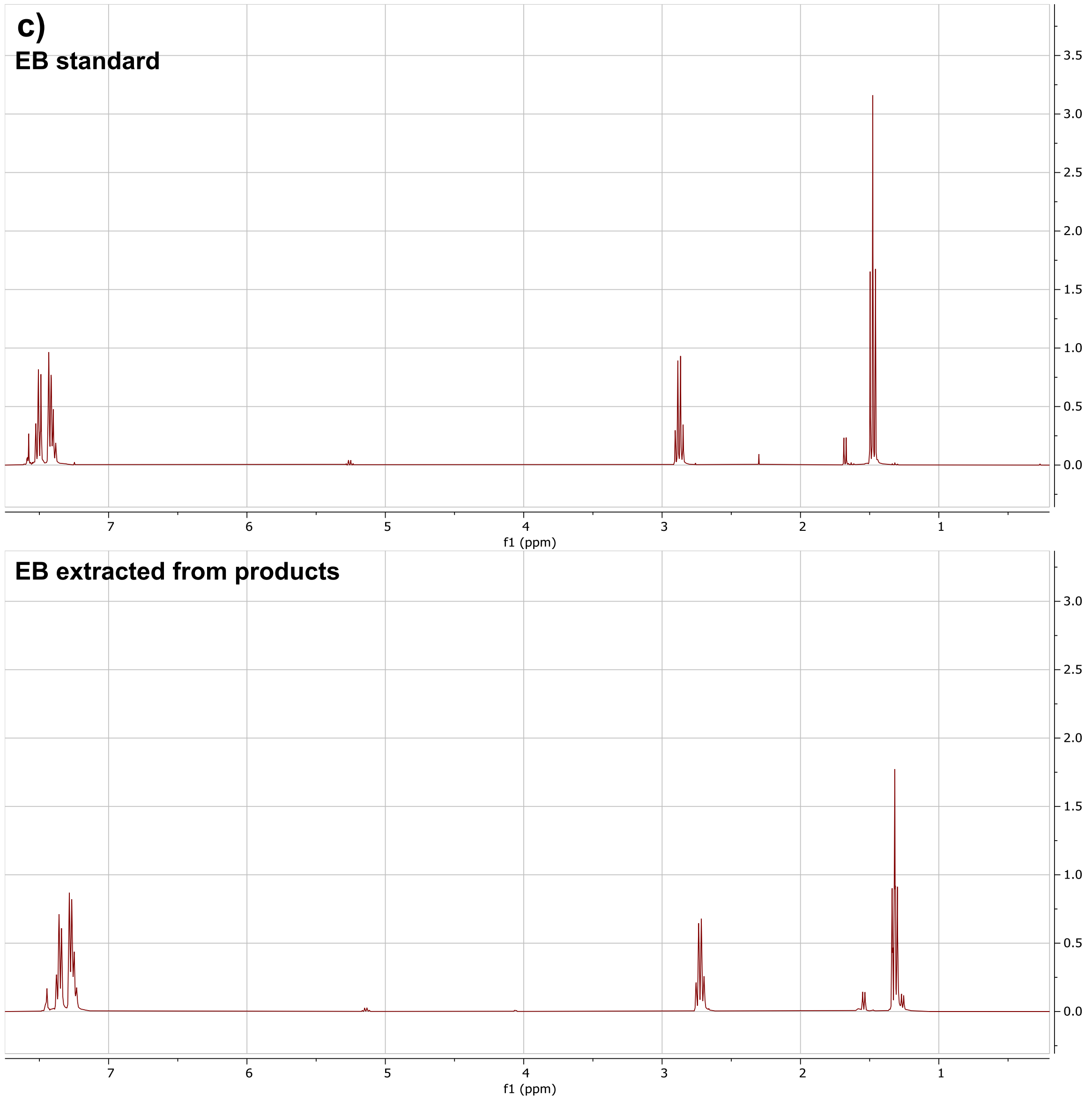


Fig. S9 ^{1}H-NMR of products a) CyOH (Cyclohexanol), b) TOL (toluene) and c) EB (ethylbenzene), isolated from the reaction mixture of BPE and PPE.

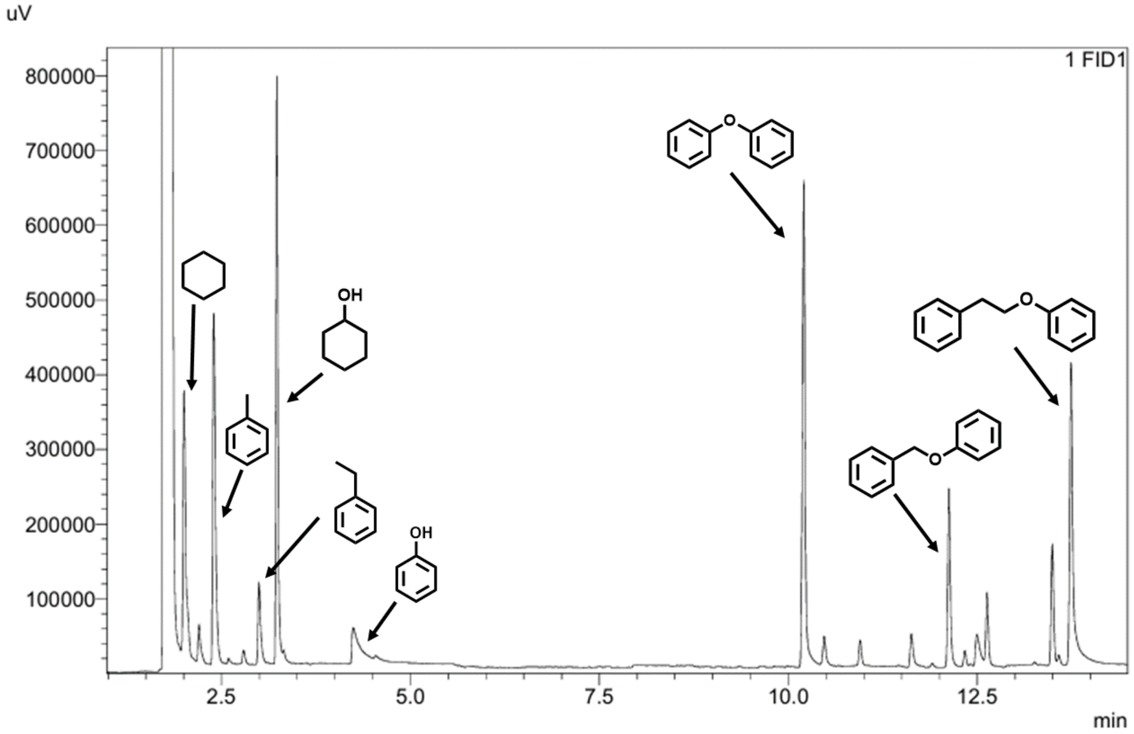


Fig. S10 GC chromatograph of obtained reaction mixture of lignin bio-oil. Reaction conditions: Simulated bio-oil (0.1 mmol), 2%Ru/ECNHS (10 mg), IPA (5 mL), H_2 (4 bar), time (3 h), 15 W blue LED.

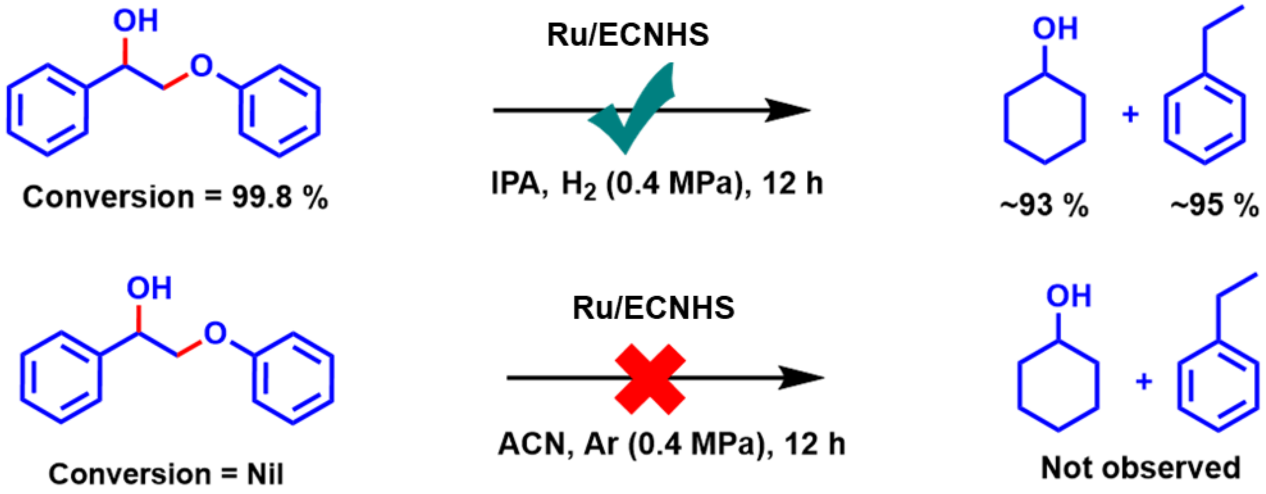


Fig. S11 Observed results under optimised photocatalytic conditions with Ru/ECNHS catalyst.

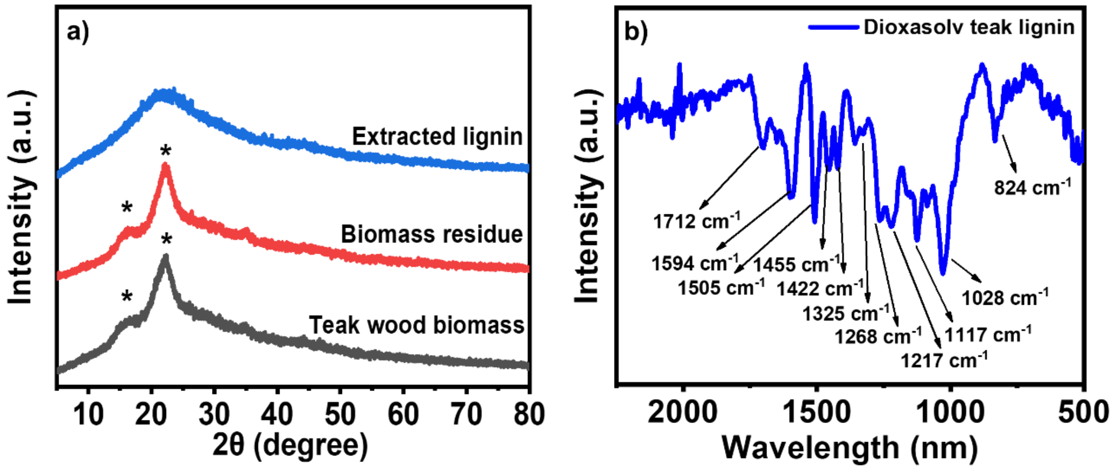


Fig. S12 a) PXRD patterns of teak wood biomass, biomass residue and extracted lignin, b) FT-IR spectra of extracted lignin.

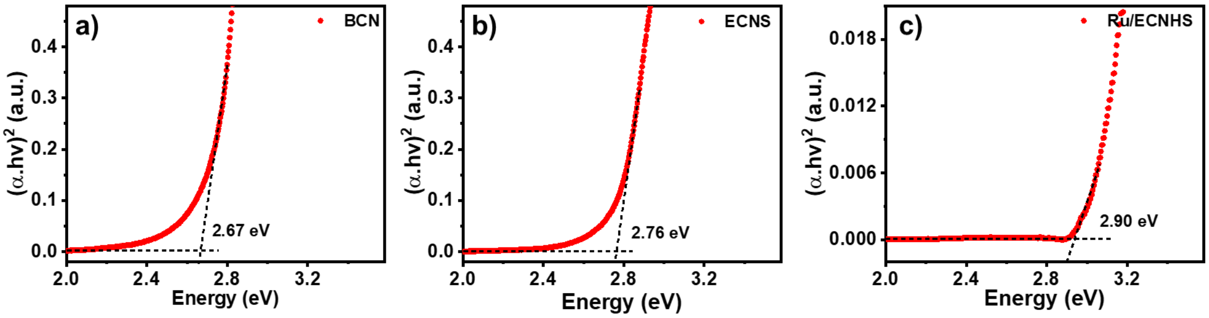


Fig. S13 Tauc plots of a) BCN, b) ECNS and c) Ru/ECNHS.

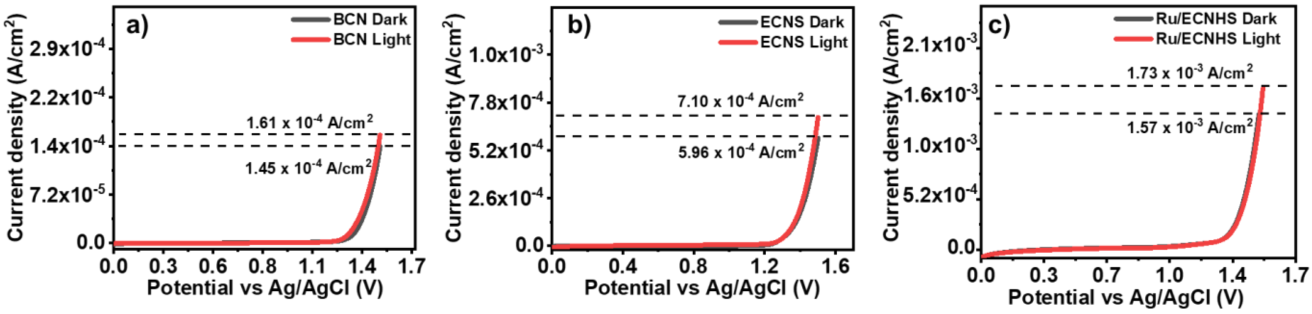


Fig. S14 LSV of a) CN, b) ECNS, c) Ru/ECNHS in light and dark conditions respectively.

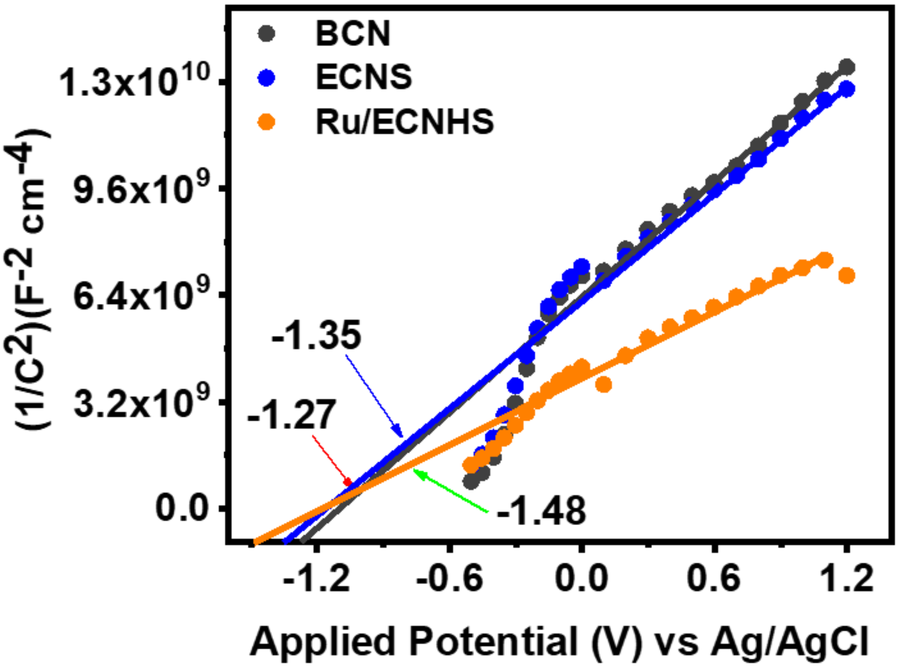
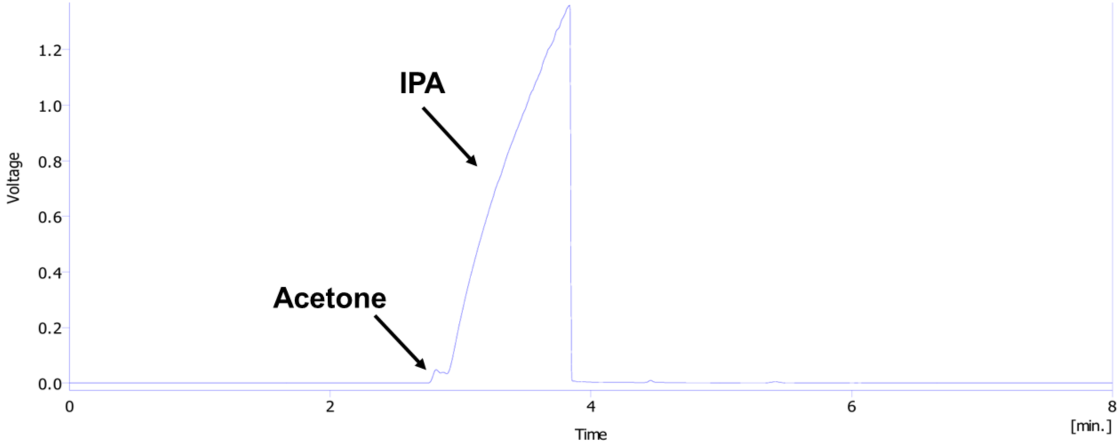
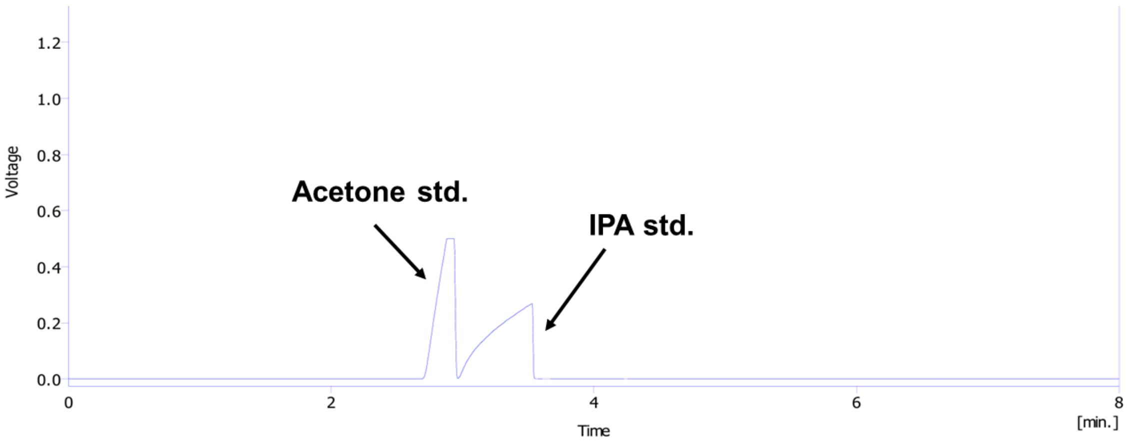


Fig. S15 MS plots of a) BCN, b) ECNS and c) Ru/ECNHS.

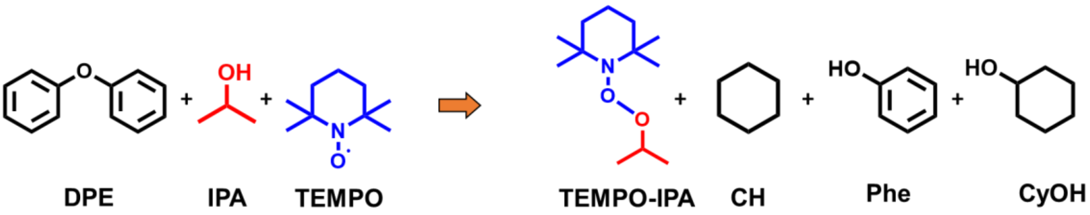




Column information – SH-I-624Sil MS Capillary, 30m x 0.25 mm x 1.40 um

GC Program – FID Temperature 290 °C, SPL Temperature 290 °C, Column – Initial temperature - 40 °C, ramp rate 5 °C/min, Final temperature 290 °C.

Fig. S16 GC chromatograph of the reaction mixture demonstrating the presence of minor amount of acetone. Reaction conditions: DPE (0.1 mmol), catalyst (10 mg), IPA (5 mL), H_2 (4 bar), time (3 h), 15 W blue LED.



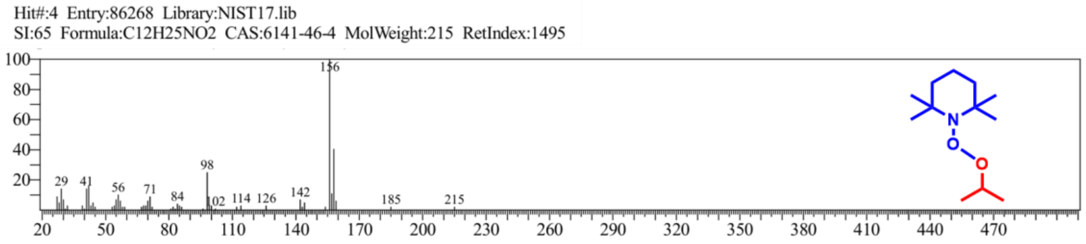


Fig. S17 Mass spectra of TEMPO-IPA intermediate.

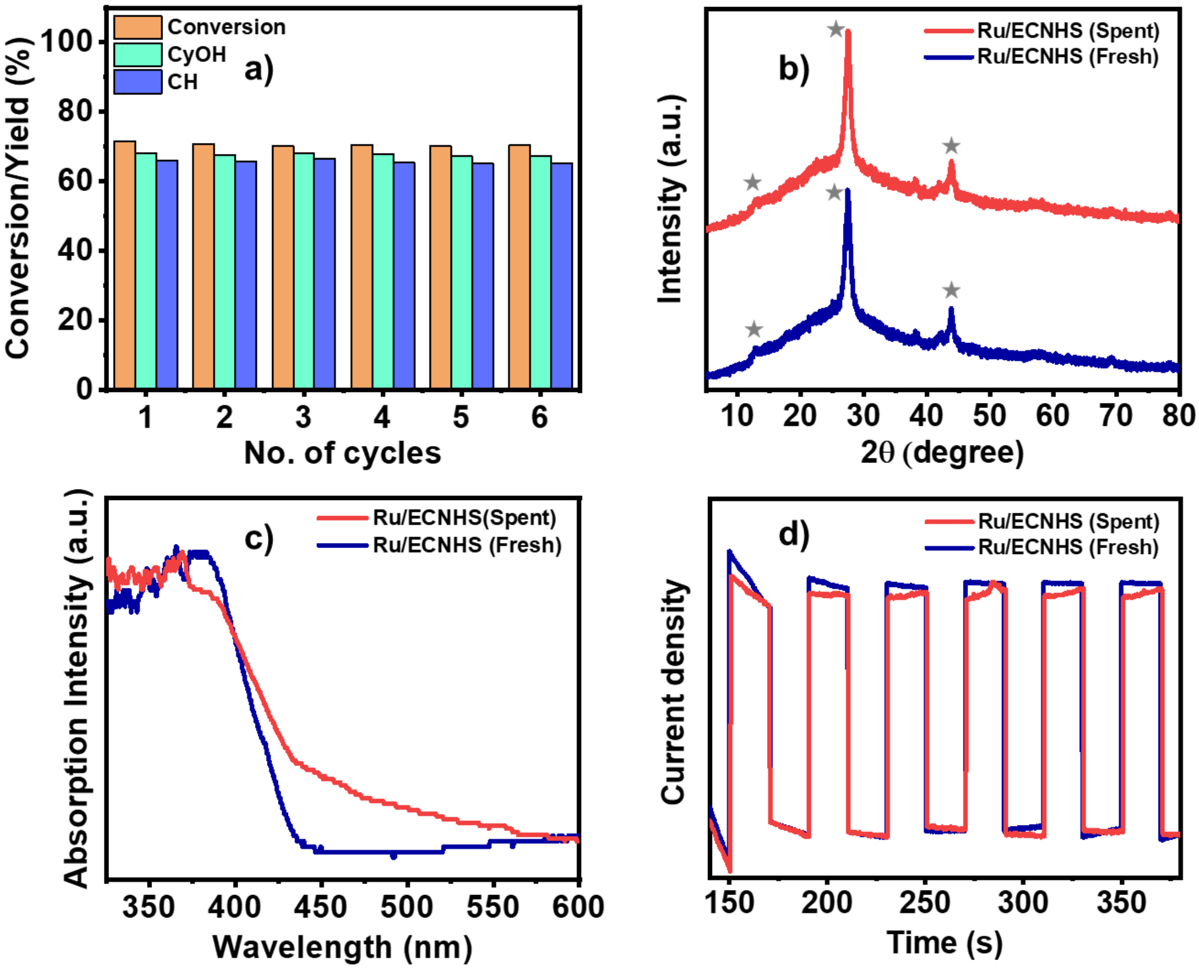


Fig. S18 a) Catalyst recyclability [Reaction conditions: DPE (0.5 mmol), catalyst amount (50 mg), IPA (10 mL), 15 W blue LED, time (3 h), H_2 (4 bar)], b) XRD, c) DR-UV spectra, d) transient photocurrent response of spent (recovered after eight cycles) and fresh catalyst.

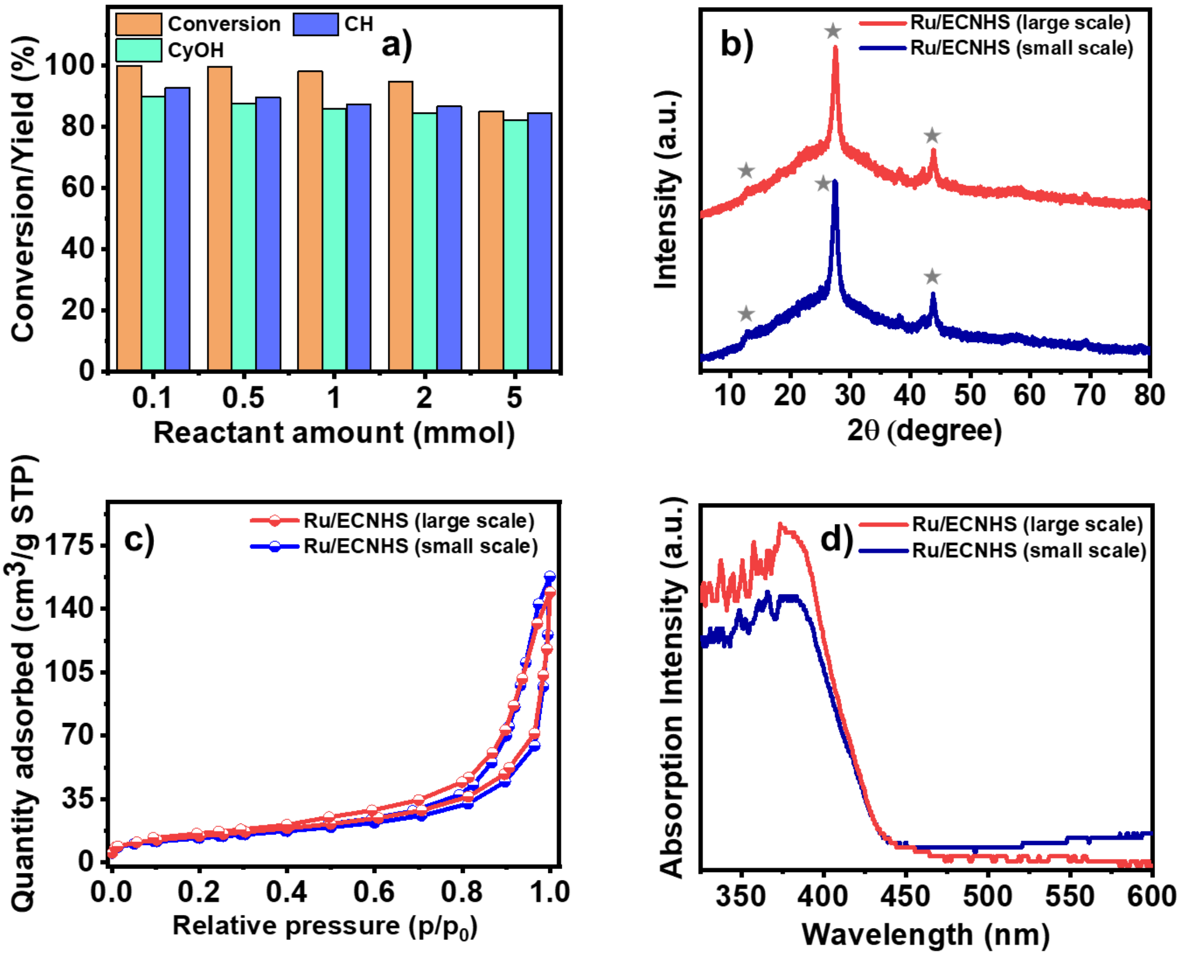


Fig. S19. a) Reaction scalability [Reaction conditions: i) For 0.1 mmol BPE: 10 mg catalyst, 3 h, IPA (5 mL), 15 W blue LED, H_2 (4 bar); ii) For 0.5 mmol BPE: 50 mg catalyst, 3 h, IPA (5 mL), 15 W blue LED, H_2 (4 bar); iii) For 1 mmol BPE: 50 mg catalyst, 6 h, IPA (5 mL), 15 W blue LED, H_2 (4 bar); iv) For 2 mmol BPE: 100 mg catalyst, 10 h, IPA (5 mL), 15 W blue LED, H_2 (4 bar); v) For 5 mmol BPE: 250 mg catalyst, 24 h, IPA (7.5 mL), 15 W blue LED, H_2 (4 bar)], b) XRD, c) N_2-sorption isotherms, d) DR-UV spectra of Ru/ECNHS (large scale) and Ru/ECNHS (small scale).

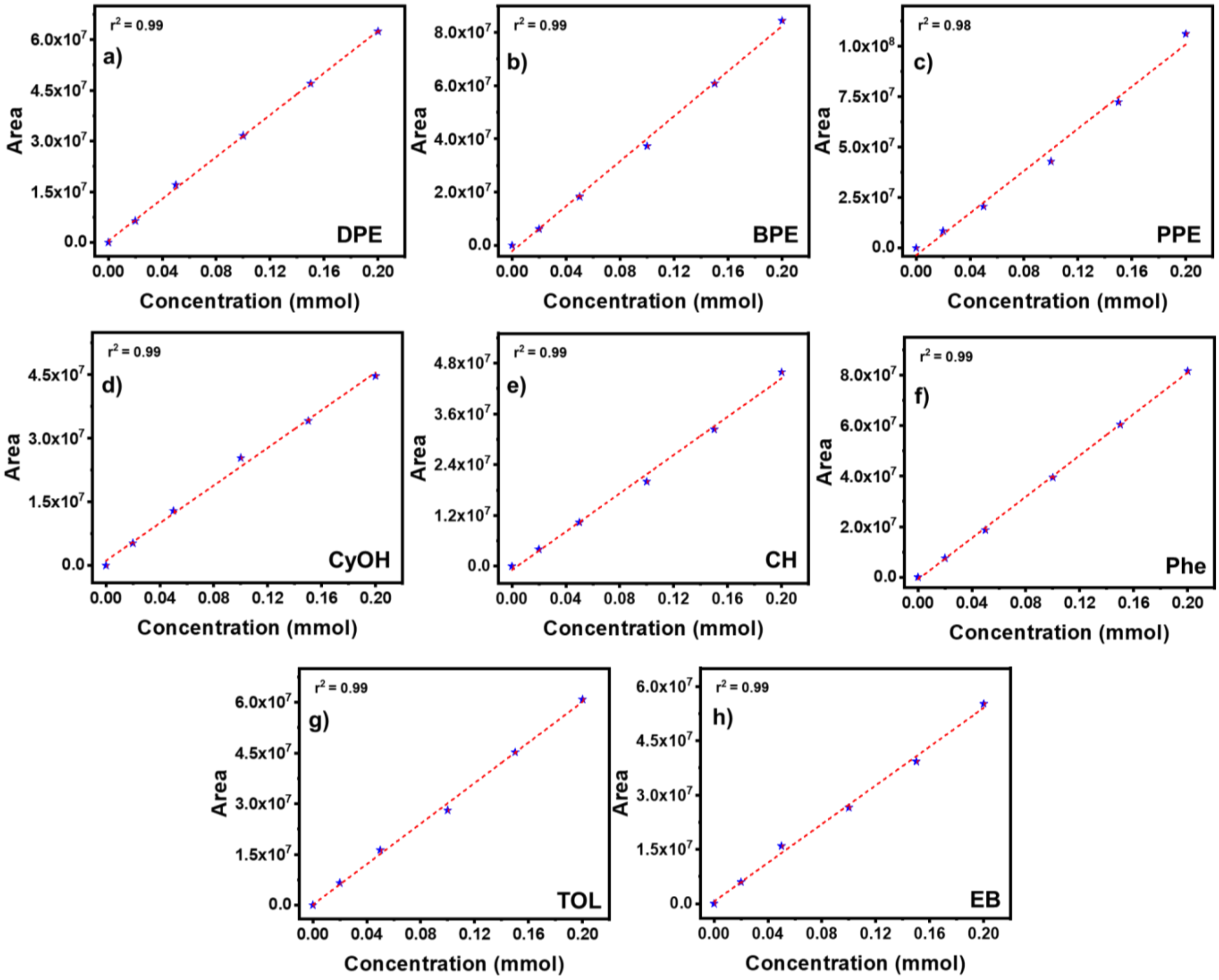


Fig. S20 GC calibration curves of a) DPE, b) BPE, c) PPE, d) CyOH, e) CH, f) Phe, g) TOL, h) EB.

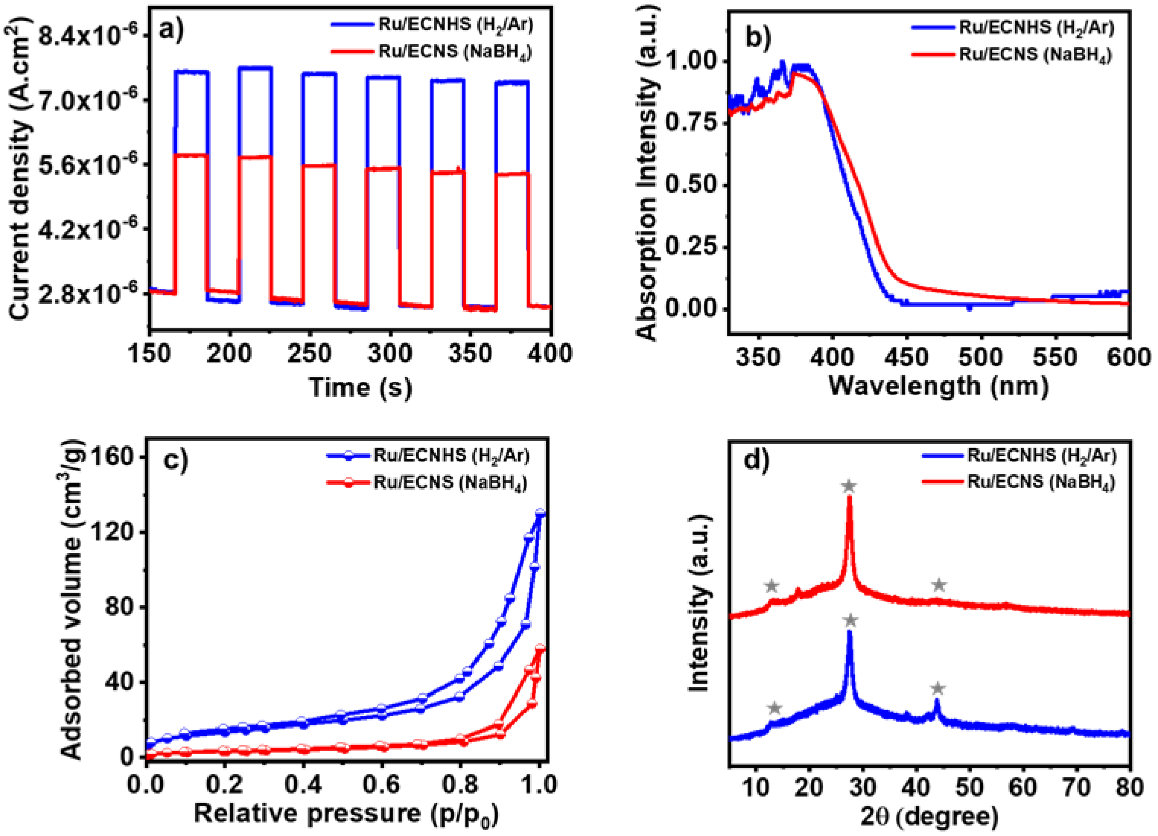
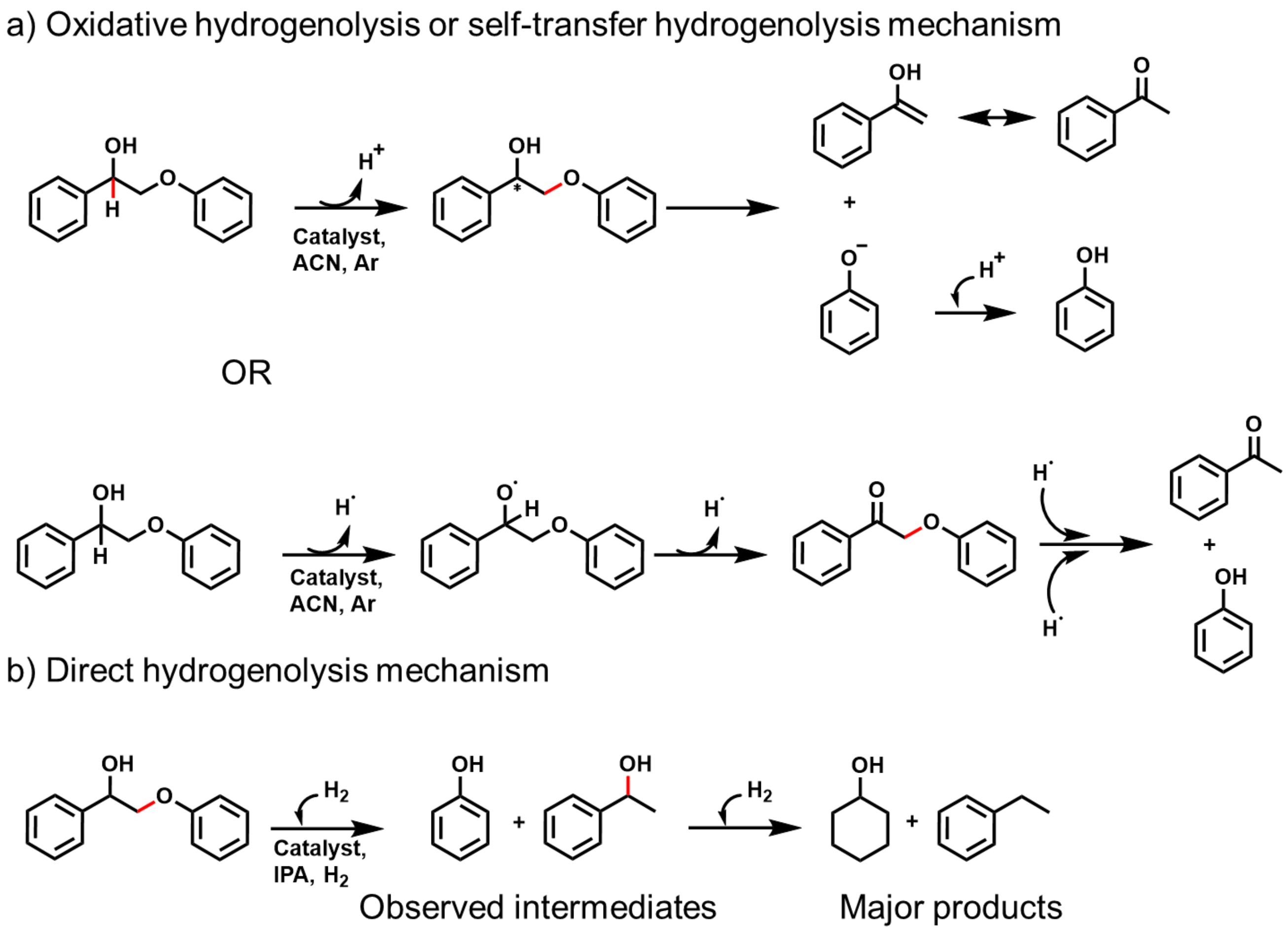


Fig. S21 a) transient photocurrent measurements, b) UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS), c) BET surface area analysis and d) XRD studies of Ru/ECNHS (H_2-Ar) and Ru/ECNS ($NaBH_4$).



Scheme S1 a) Oxidative hydrogenolysis or self-transfer hydrogenolysis mechanism, and b) Direct hydrogenolysis mechanism of PPEOL.

References:

1 R. Ghalta, R. Bal and R. Srivastava, *Green Chem.*, 2023, **25**, 7318–7334.

2 Q. He, M. Worku, L. Xu, C. Zhou, S. Lteif, J. B. Schlenoff and B. Ma, *J. Mater. Chem. A*, 2020, **8**, 2039–2046.

3 K. Gelderman, L. Lee and S. W. Donne, *J. Chem. Educ.*, 2007, **84**, 685.

4 S. Hoang, S. Guo, N. T. Hahn, A. J. Bard and C. B. Mullins, *Nano Lett.*, 2012, **12**, 26–32.

5 R. Ghalta and R. Srivastava, *Green Chem.*, 2024, **26**, 7384–7405.

6 S. Han, Y. Zhao, M. Liang, X. Zhai, Q. Zhang, N. Sun, R. Ma, G. Li, Z. Xiao and Z. Ni, *Green Chem.*, 2025, **27**, 8883–8900.

7 Z. Peng, Z. Wu, X. Sun and H. Li, *Green Chem.*, 2023, **25**, 6869–6880.