

Supporting Information

**Photo-Induced Oxidative Degradation of Polystyrene Waste by
Surface Modified Heterogeneous Titanium Catalyst under Air**

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1. Instrumentation

Powder XRD measurement was carried out using Empyrean 3rd Gen, Malvern PANalytical X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The incident beam operated at 40 kV and 40 mA in 2θ mode with scan range 10° - 80° and scan rate $10^\circ \text{ min}^{-1}$. FESEM analysis was performed with model number NOVA NANOSEM 450 attached with energy dispersive X-ray analysis (EDX) to determine the elemental composition. FEI Tecnai G2, F30 instrument with accelerating potential 300 kV was utilized for HRTEM study. For reducing the particle size, TiO_2 powder was ultra sonicated by Sonics Vibra Cell probe sonicator. XPS characterization was performed using Kratos Analytical model no. Axis Supra+ X-ray photometer with a capacity of 1486.6 eV Al $\text{K}\alpha$ radiation. Gel Permeation Chromatography (GPC) was performed on Shimadzu GPC Sedex 85 LT- ELSD with Semi preparative LC-20AR HPLC system. THF was used as an eluent at a flow rate of 1.0 mL/min at room temperature. EPR spectra were recorded at 120K on a Bruker EMX-9.5/12 spectrometer. UV-Vis spectra were recorded using Shimadzu UV-1780 spectrophotometer. IR spectrums were recorded on a Shimadzu 0459 spectrometer in ATR mode. ^1H and ^{13}C NMR spectrums were obtained on JEOL JNM-LA 500 MHz and JEOL JNM-LA 400 MHz spectrometers. Chemical shift values were referenced to the residual signals of the deuterated solvents. Energy Dispersive X-Ray Fluorescence (ED-XRF) analysis, conducted on a Wavelength Dispersive X-Ray Fluorescence spectrophotometer Bruker X8 Tiger. ESI-MS were recorded on a Waters Micro mass Quattro Micro triple-quadruple mass spectrometer. GC-MS studies were carried out using an Agilent 7890A GC and 5975C MS system.

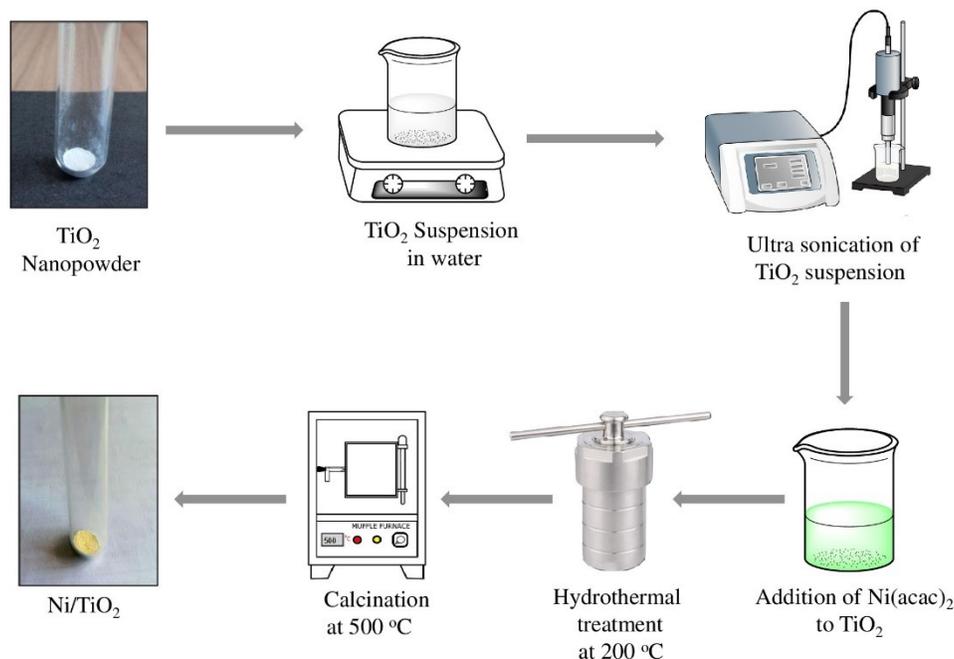
2. Materials

PS and its different derivatives are collected from local plastic recycle bin. Commercial TiO_2 nanopowder (purity 99%) was purchased from Ad-Nano Technologies Pvt. Ltd., India. Metal precursor $\text{Ni}(\text{acac})_2$, TEMPO, BHT, TEA, AcOH, and DMPO were purchased from Thermo Fisher Scientific. The $\text{Ni}(\text{acac})_2$ was heated at 80°C for 3 h under vacuum prior to use. *p*-Benzoquinone and PivOH were purchased from BLD Pharm and stored under vacuum desiccators. Deuterated solvent CDCl_3 (99.8 atom % D) for NMR was purchased from Sigma-Aldrich. All the HPLC grade solvents (99.99 % pure) such as ethyl acetate, acetonitrile, ethanol, THF, acetone, and pet ether were purchased from SRL Laboratories and dried using standard solvent drying procedure. Deuterated pivalic acid (PivOD) is prepared according to literature procedure.¹ Inorganic acids like H_2SO_4 , HNO_3 , and *o*- H_3PO_4 were purchased from Merck Life Science.

3. Synthesis of Ni/TiO₂

A suspension of TiO_2 nanopowder (100 mg) was prepared with 60 mL distilled water and then ultra sonicated using probe sonicator for 20 min. Then 5 mg $\text{Ni}(\text{acac})_2$ precursor was dissolved in 2 mL ethanol and it was added dropwise to the TiO_2 suspension over 10 min. The reaction mixture was kept under stirring for 1.5 hours. Next, the dispersion was heated at 200°C for 18 h under a teflon-lined stainless steel autoclave. The solid was collected by filtration after cooling to room temperature and washed with

distilled water. The resultant solid was dried over hot plate and then it was calcinated at 500 °C using a muffle furnace for 2 h and finally Ni/TiO₂ was obtained as light yellow solid. The wt. % of Ni was determined by EDX analysis which indicates 1.15 wt. % Ni doping on TiO₂ surface. The obtained Ni/TiO₂ was well characterized by several experimental techniques.



Scheme S1. Preparation of Ni/TiO₂ by hydrothermal method.

4. EDX analysis for elemental composition

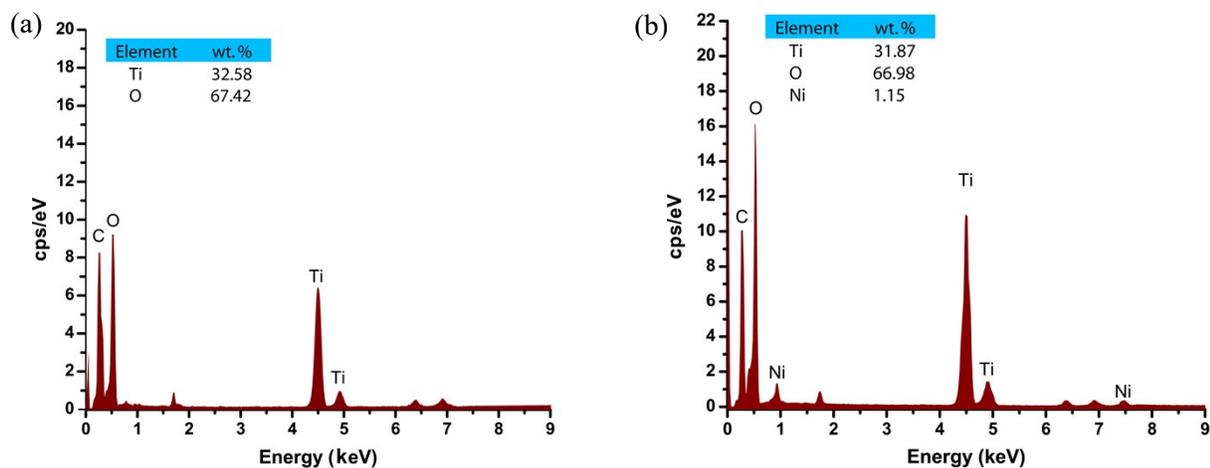


Figure S1. EDX analysis for the determination of elemental compositions of (a) TiO₂ and (b) Ni/TiO₂. Carbon peak is appeared here due to carbon coating on the sample.

5. SAED analysis and lattice spacing for materials

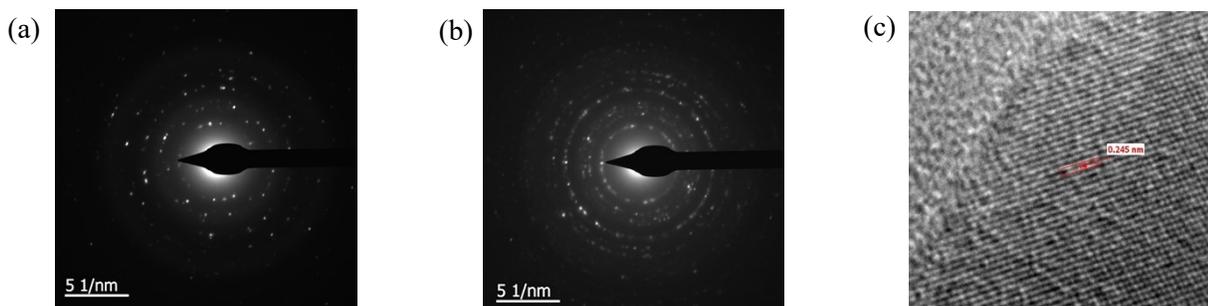


Figure S2. SAED pattern for (a) TiO₂ and (b) Ni/TiO₂. (c) Determination of crystal lattice spacing (d spacing) for Ni/TiO₂.

6. Surface characterization by XPS

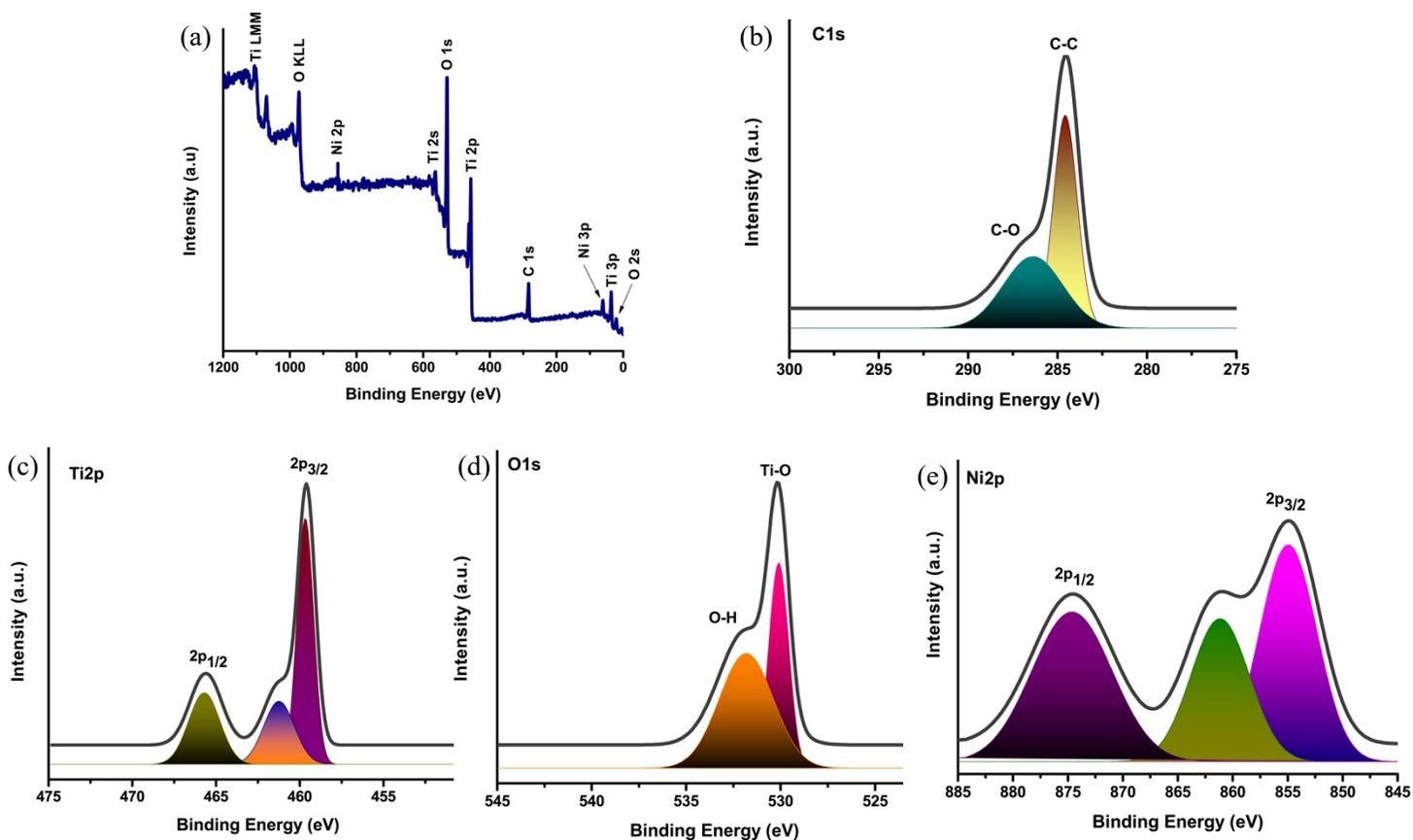


Figure S3. (a) XPS survey scan (0-1200 eV) of Ni/TiO₂ where C 1s peak is calibrated at 284.6 eV. Deconvoluted spectra of high resolution XPS scan of (b) C 1s, (c) Ti 2p, (d) O 1s, and (e) Ni 2p region.

7. UV-Vis studies

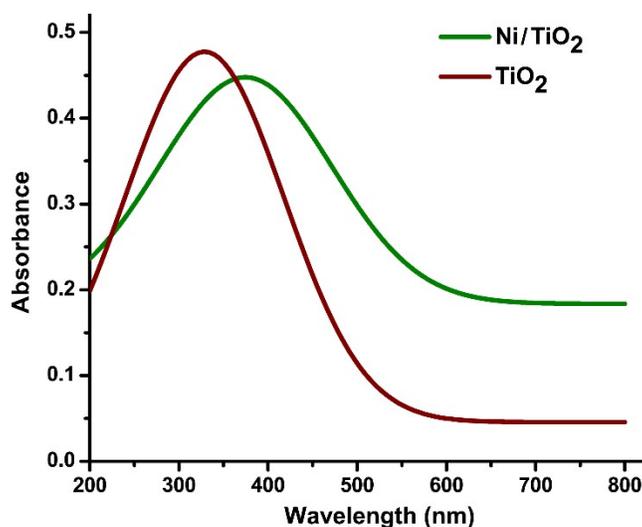


Figure S4. UV-Vis absorption spectra of TiO₂ and Ni/TiO₂ in water.

8. Calculation of no. of moles for PS²

$$\text{No. of moles of PS (n}_{\text{ps}}) = \frac{\text{Weight of PS taken}}{\text{Molecular weight of styrene monomer}} \quad \text{..... eq.1}$$

9. General procedure for photoinduced breakdown of PS

For ketone formation, a catalytic vessel was charged with 35 mg of PS sample (0.34 mmol, corresponds to styrene monomer) and dissolved in 2 mL ethyl acetate. Then 10 mg Ni/TiO₂ catalyst was added and followed by addition of PivOH (69 mg, 0.68 mmol) into the reaction mixture. The vessel was placed inside the photoreactor and irradiated with 10W blue LED light (450 nm). The blue LED created a local temperature 40 ± 2 °C around the reactor. The reaction mixture was kept under stirring for 12h. After that, reaction mass was filtered and 10 mL of distilled water was added into it. Organic products were extracted with ethyl acetate, washed with brine solution, and dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and crude product was purified by flash column chromatography on silica gel. The isolated product was characterized by ¹H, ¹³C NMR spectroscopy and ESI-MS, found *m/z* (*z* = 1) value 121.08 corresponds to [M+H]⁺.

For acid formation, PivOH (139 mg, 1.36 mmol) was used and other parameters kept unchanged as mentioned in ketone formation. After the reaction, solvent was evaporated in vacuo. Then 5 mL 2N NaOH was added into the resultant solid followed by stirring for few minutes. Next, the solution was filtered to remove undissolved parts and filtrate was collected in 25 mL beaker. Then filtrate was acidified with 4N HCl by adjusting pH 3 of the solution to afford white precipitate. It was collected by filtration

and dried under air. Finally, obtained white solid was purified by recrystallization. The isolated product was characterized by ^1H , ^{13}C NMR spectroscopy and ESI-MS, found m/z ($z = 1$) value corresponds to [M-H] $^-$.

10. Optimization of reaction condition

Table S1. Optimization of reaction conditions^[a]

PS $\xrightarrow[\text{Air, rt, 12 h}]{\text{Catalyst, Acid, Blue LED (450 nm), Solvent (2mL)}}$ 1 + 2 + 3

Entry	Catalyst	Acid (equiv.)	Solvent	% Yield ^[b]		
				1	2	3
1 ^[c]	Ni/TiO ₂	PivOH (1)	EtOAc	24	9	5
2 ^[c]	TiO ₂	PivOH (1)	EtOAc	nd ^[e]	nd ^[e]	nd ^[e]
3	Ni/TiO ₂	PivOH (2)	EtOAc	55	8	nd^[e]
4	Ni/TiO ₂	PivOH (4)	EtOAc	6	57	nd^[e]
5	Ni/TiO ₂	PivOH (3)	EtOAc	40	19	nd ^[e]
6	Ni/TiO ₂	PivOH (5)	EtOAc	7	54	5
7	Ni/TiO ₂	AcOH (2)	EtOAc	4	3	2
8	Ni/TiO ₂	AcOH (4)	EtOAc	5	6	3
9	Ni/TiO ₂	H ₂ SO ₄ (2)	EtOAc	17	22	6
10	Ni/TiO ₂	H ₂ SO ₄ (4)	EtOAc	22	29	4
11	Ni/TiO ₂	HNO ₃ (2)	EtOAc	15	22	7
12	Ni/TiO ₂	HNO ₃ (4)	EtOAc	21	23	3
13	Ni/TiO ₂	HCl (2)	EtOAc	24	12	4
14	Ni/TiO ₂	HCl (4)	EtOAc	18	21	5
15	Ni/TiO ₂	H ₃ PO ₄ (2)	EtOAc	6	10	2
16 ^[d]	-	PivOH (2)	EtOAc	nd ^[e]	nd ^[e]	nd ^[e]
17 ^[f]	Ni/TiO ₂	-	EtOAc	7	8	nd ^[e]
18	Ni/TiO ₂	PivOH (2)	Benzene	15	11	3
19	Ni/TiO ₂	PivOH (2)	Pet Ether	16	9	4
20	Ni/TiO ₂	PivOH (2)	Cyclohexane	12	9	7
21	Ni/TiO ₂	PivOH (2)	CH ₃ CN	36	13	5
22	Ni/TiO ₂	PivOH (4)	CH ₃ CN	10	41	4
23	Ni/TiO ₂	PivOH (2)	THF	32	12	8
24	Ni/TiO ₂	PivOH (4)	THF	11	38	6
25	Ni/TiO ₂	PivOH (2)	Acetone	23	21	5
26	Ni/TiO ₂	PivOH (2)	CH ₃ CN/ THF (1:1 v/v)	12	18	7
27	Ni/TiO ₂	PivOH (2)	CH ₃ CN/ EtOAc (1:1 v/v)	39	13	10
28	Ni/TiO ₂	PivOH (2)	CH ₃ CN/ H ₂ O (1:1 v/v)	11	9	nd ^[e]
29	Ni/TiO ₂	PivOH (2)	THF/ H ₂ O (1:1 v/v)	8	6	11

^[a]Reactions were carried out using PS foam (0.34 mmol), catalyst (10 mg), and acid (measured equiv.) in 2 mL solvent for 12 h stirring in air under blue LED (450 nm, 10W) irradiation. Blue LED created a local temperature 40 ± 2 °C. ^[b]Yields were determined by GC-MS using mesitylene as an internal standard. ^[c]15 mg catalyst was used. ^[d]Reaction was performed without catalyst. ^[e]Product not detected. ^[f]Reaction was performed without PivOH.

11. Recycling of Ni/TiO₂

After 1st photodecomposition test, the used Ni/TiO₂ catalyst was collected by filtration. It was then dispersed on THF and stirred for 5 min in room temperature, followed by heating at 50 °C for 2h. Then mixture was subsequently filtered again, washed with pet ether, and solid residue was dried in air for further use.

12. Calculation of E factors³

$$E \text{ (Environmental) Factor} = \frac{\text{Total mass of waste}}{\text{Total mass of product(s)}} \quad \dots \text{eq.2}$$

Table S2. Determination of E factors for each reaction with recycled catalyst^a

Acetophenone Formation ^b				Benzoic Acid Formation ^b			
No. of Cycle	Waste (mg)	Product (mg)	E Factor	No. of Cycle	Waste (mg)	Product (mg)	E Factor
1	8.5	26.5	0.32	1	8.1	26.9	0.30
2	9.4	25.6	0.36	2	8.9	26.1	0.34
3	10.6	24.4	0.42	3	10.2	24.8	0.41
4	11.9	22.5	0.53	4	11.8	23.1	0.51
5	12.1	22.7	0.53	5	12.2	22.6	0.54
6	13.2	21.8	0.60	6	13.1	21.9	0.59

^aCatalyst is recyclable and solvent is extractable. Hence, these are excluded from the calculation.

^bCalculations were performed based on 0.35 mmol reactant scale.

13. GPC chromatogram of different PS derivatives

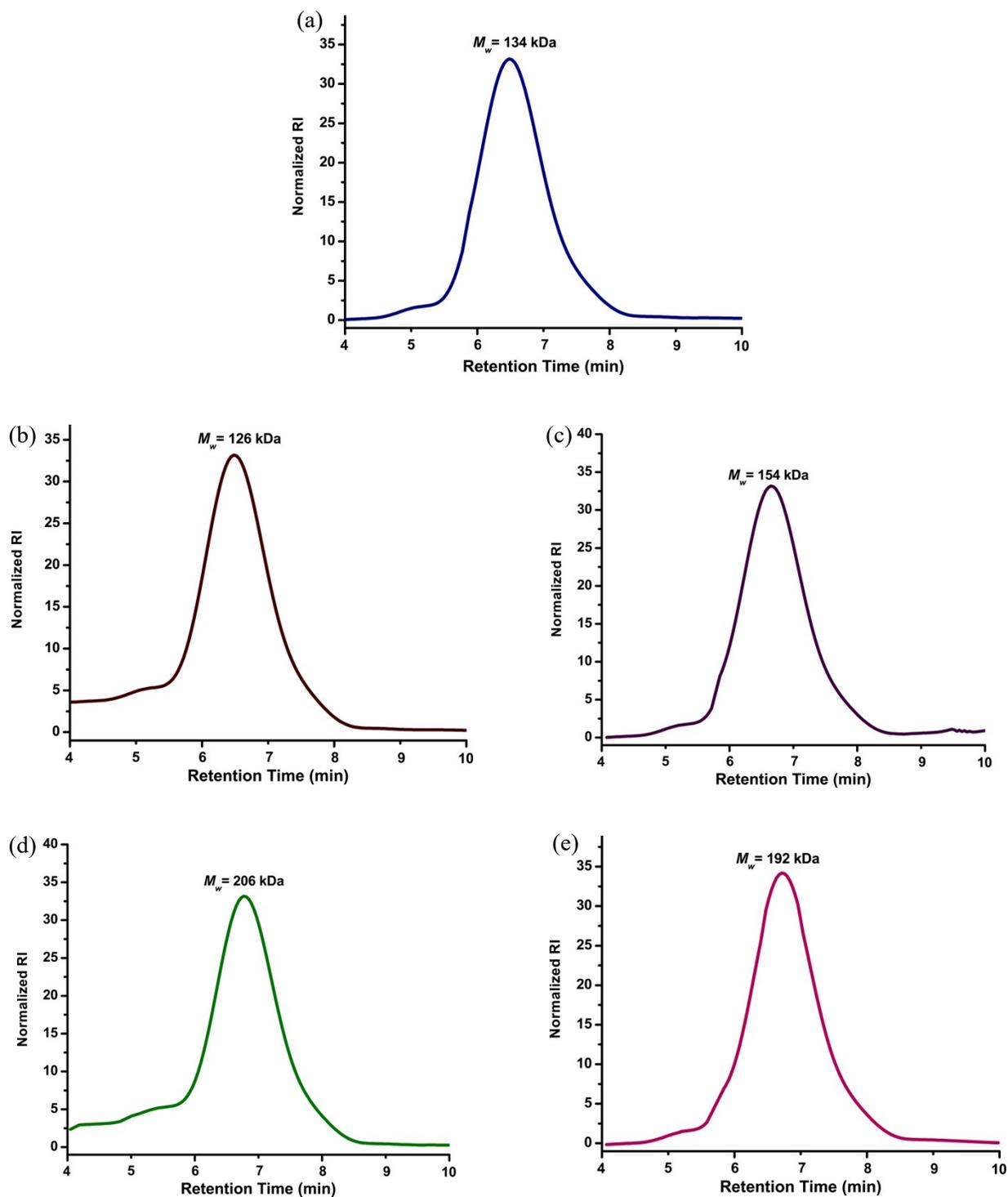


Figure S5. GPC chromatogram of (a) EPS foam, (b) thermocol sheet, (c) food box, (d) packaging material, and (e) disposable bowl.

14. General procedure for time dependent ATR-IR

A catalytic vessel was charged with 52 mg PS foam and dissolved in 2.5 mL of EtOAc solvent. Next, 11 mg Ni/TiO₂ catalyst and followed by 98 mg PivOH were added into the reaction mixture. The reaction vessel was placed inside the photoreactor under air and 10W blue LED irradiation. 0.5 mL Aliquot was taken out and filtered through 0.22 μm microfilter to remove the catalyst and washed with 1 mL EtOAc. Then EtOAc was evaporated under reduced pressure and pet ether was added into it. In the next step, pet ether solution was washed repeatedly with water to remove excess PivOH. Finally, pet ether was removed by solvent evaporation and crude reaction mass was analyzed by ATR-IR.

15. Mass balance

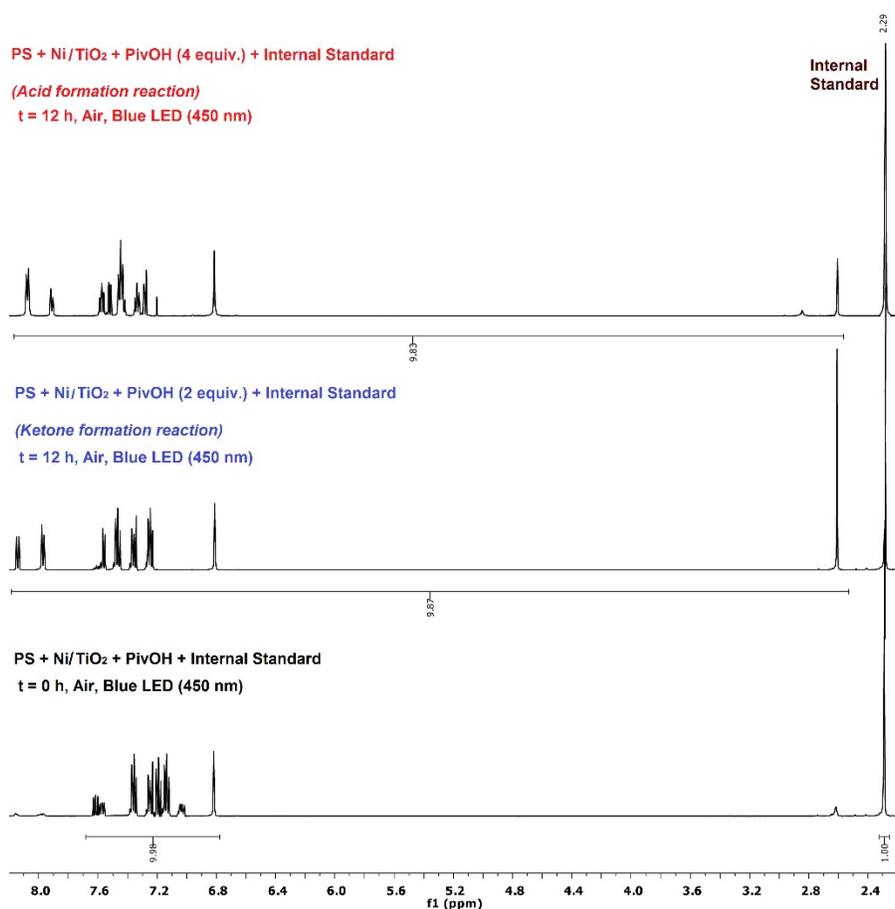


Figure S6. ¹H NMR spectra including integration results of starting material (aromatic region) and at the end of reaction after 12 h (aromatic and aliphatic region 2.59-8.3 ppm) at standard reaction condition that shows mass balance of the reaction. The singlet peak at 2.29 ppm originates from mesitylene was set as 1 for integration. Mass balance for ketone formation and acid formation reaction are found to be 98.89% and 98.49%, respectively.

16. Isotope labeling experiment

A catalytic vessel was charged with 50 mg PS foam and dissolved in 2 mL of EtOAc solvent. Next, 10 mg Ni/TiO₂ catalyst and followed by 98 mg PivOD were added into the reaction mixture. The reaction vessel was placed inside the photoreactor under air and 10W blue LED irradiation for 12 h. At the end of reaction, crude mass was filtered and washed with brine solution. The desired product was isolated by column chromatography on silica gel. Finally, product was characterized by ESI-MS and ¹H NMR.

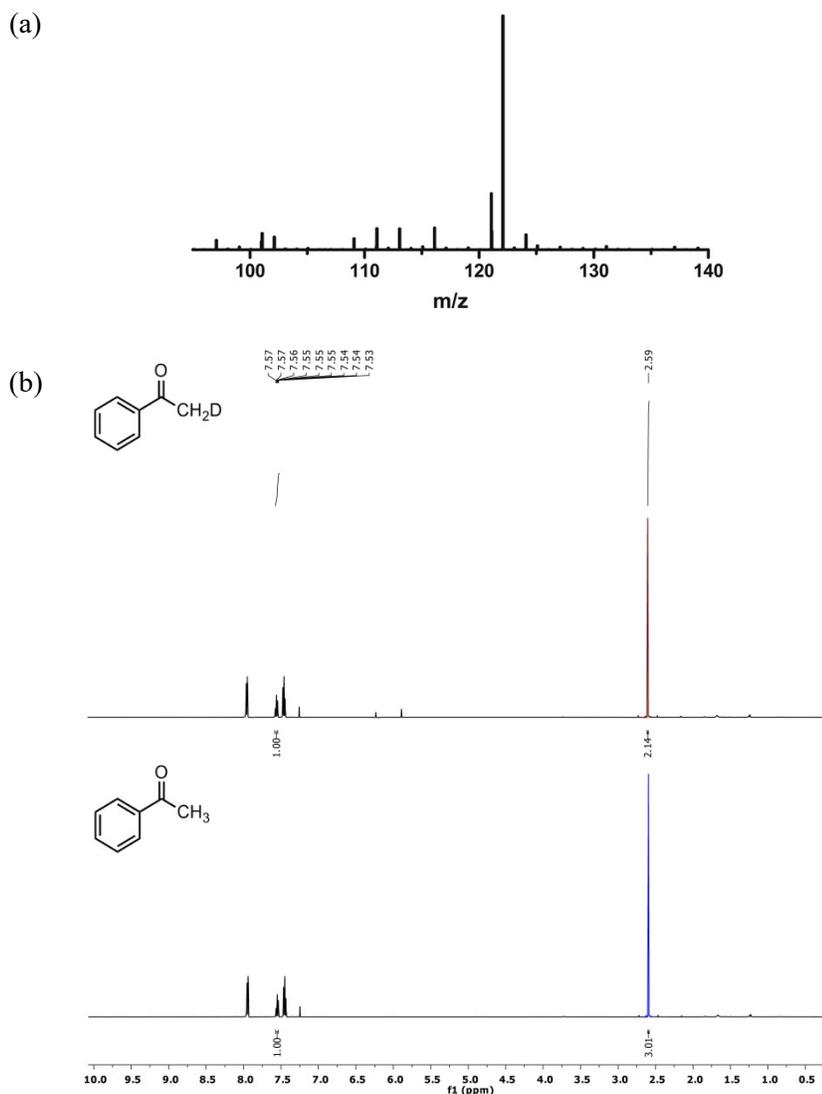


Figure S7. (a) ESI-MS for molecular ion at $m/z = 122.14$ ($z = 1$) corresponds to $[M+H]^+$ where $M = C_8H_7DO$. (b) ¹H NMR (400 MHz, CDCl₃) of acetophenone-*d*₁ and acetophenone. D atom incorporation in methyl group of acetophenone-*d*₁ is 28.7%.

17. ED-XRF analysis

Table S3. ED-XRF analysis of Ni/TiO₂ at 1st and 6th reaction cycle

Cycle	%Ti	%Ni	% Others impurities (Si, Fe & Al)
1	98.819	1.16	0.021
6	96.714	0.76	2.526

18. Analysis of recycled catalyst

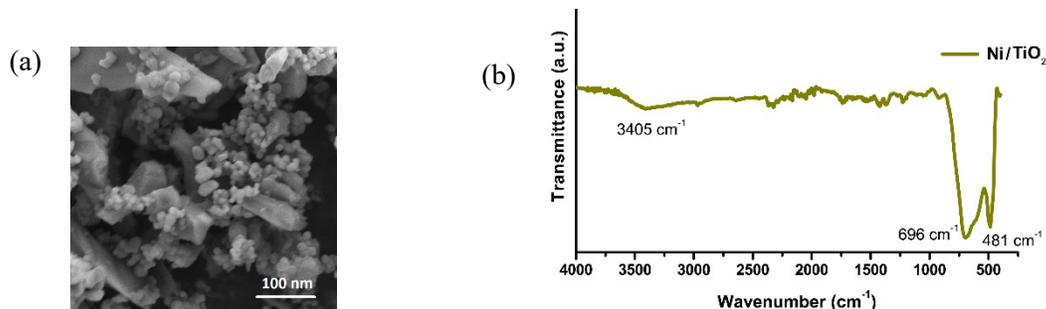


Figure S8. (a) FESEM image and (b) ATR-IR of recycled Ni/TiO₂ after 6th reaction cycle.

19. Control experiments

Table S4. Control experiments for mechanistic studies

Entry	Deviation /addition w.r.t standard condition	% Yield ^[a]		
		1	2	3
<i>Effect of air</i>				
1	None	55	8	0
2	N ₂ instead of air	0	0	0
<i>Intermediacy of radical species</i>				
3	Addition of TEMPO (2 equiv.)	3	1	0
4	Addition of BHT (2 equiv.)	0	0	0
<i>Hole scavenger</i>				
5	Addition of TEA (2 equiv.)	0	0	0
<i>Tracing of active oxygen species</i>				
6	Addition of <i>p</i> -benzoquinone (2 equiv.)	2	0	0
<i>Reaction pathway analysis for acid formation</i>				
7	Acetophenone (0.34 mmol) instead of PS	-	0	0

^[a]Yields were determined by GC-MS using mesitylene as an internal standard.

20. Spin trap EPR

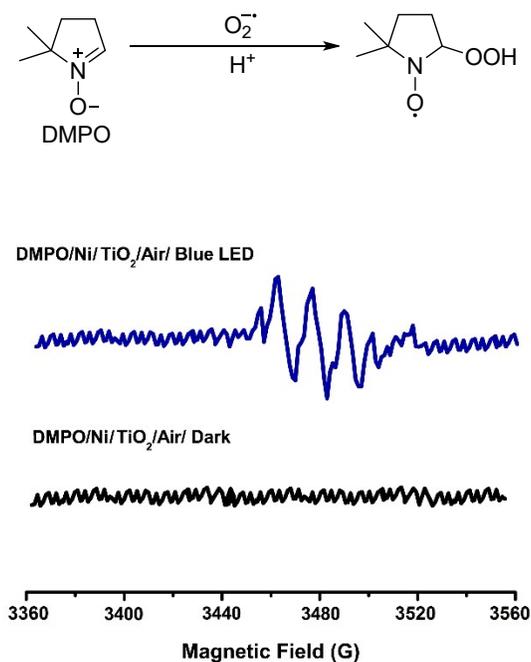


Figure S9. Spin trap EPR by DMPO in the presence and absence of blue light at 120K.

21. Calculation of GC-MS yield⁴

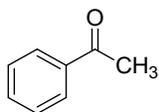
Analysis of catalytic reactions was carried out by GC-MS and product yields were determined using by GC-MS using mesitylene as an internal standard (IS). Equimolar amount of mesitylene IS with respect to reactant PS was added to the reaction mass prior to analysis. Calibrations were carried out to obtain the relative response factors (RF) of the products compared to IS.

$$RF = \frac{\text{Area}_{IS} \times \text{Moles}_{\text{Analyte}}}{\text{Area}_{\text{Analyte}} \times \text{Moles}_{IS}} \dots\dots eq.3$$

$$\text{Moles}_{\text{Product}} = \frac{RF \times \text{Moles}_{IS} \times \text{Area}_{\text{Product}}}{\text{Area}_{IS}} \dots\dots eq.4$$

$$\% \text{ Yield} = \frac{\text{Moles}_{\text{Product}}}{\text{Moles}_{\text{Reactant}}} \times 100 \dots\dots eq.5$$

22. ¹H and ¹³C NMR of products



¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.96-7.94 (m, 2H, ArH), 7.57-7.53 (m, 1H, ArH), 7.47-7.43 (m, 2H, ArH), 2.59 (s, 3H, -CH₃); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 198.28, 137.17, 133.19, 128.64, 128.38, 26.70.

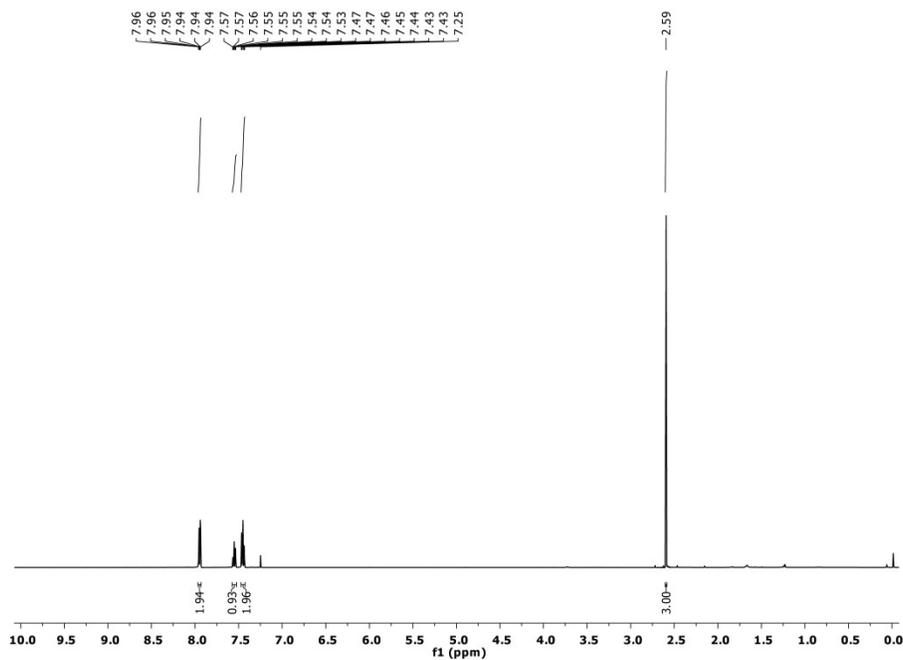


Figure S10. ¹H NMR (500 MHz, CDCl₃) of acetophenone.

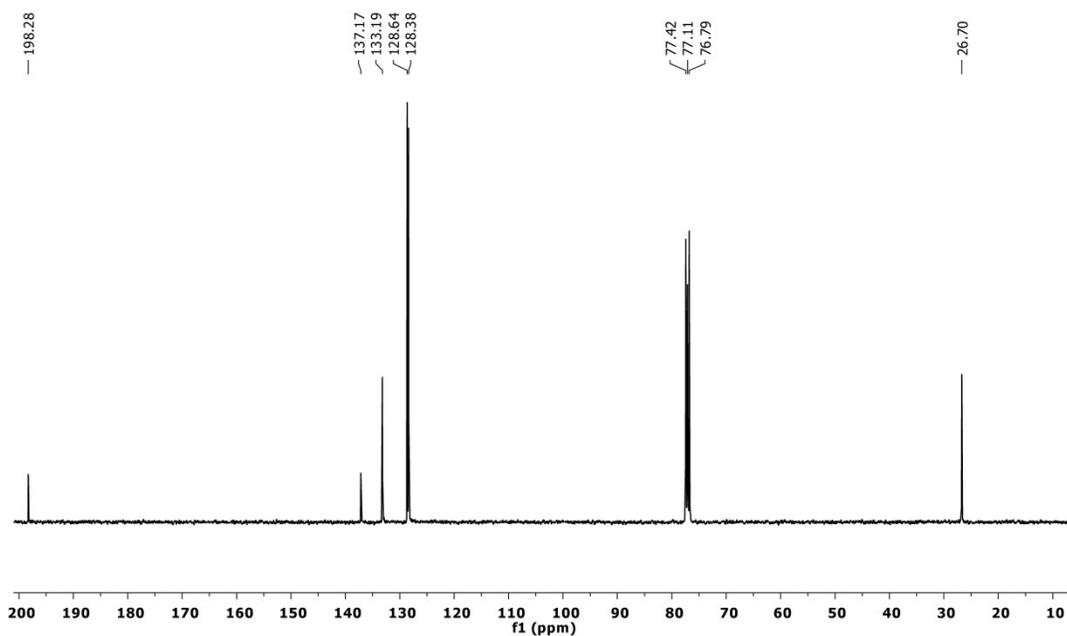
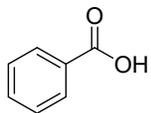


Figure S11. ¹³C NMR (125 MHz, CDCl₃) of acetophenone.



^1H NMR (400 MHz, CDCl_3): δ (ppm) = 11.82 (brs, 1H, -COOH), 8.13 (d, 2H, $J = 7.4$ Hz, ArH), 7.61 (t, 1H, $J = 7.4$ Hz, ArH), 7.48 (t, 2H, $J = 7.7$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 172.54, 133.91, 130.30, 129.39, 128.57.

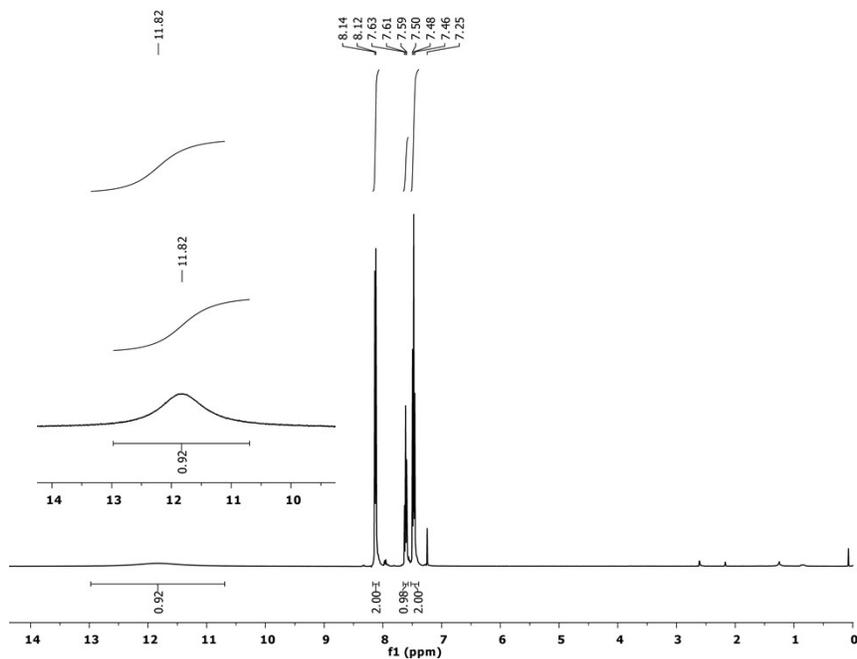


Figure S12. ^1H NMR (400 MHz, CDCl_3) of benzoic acid.

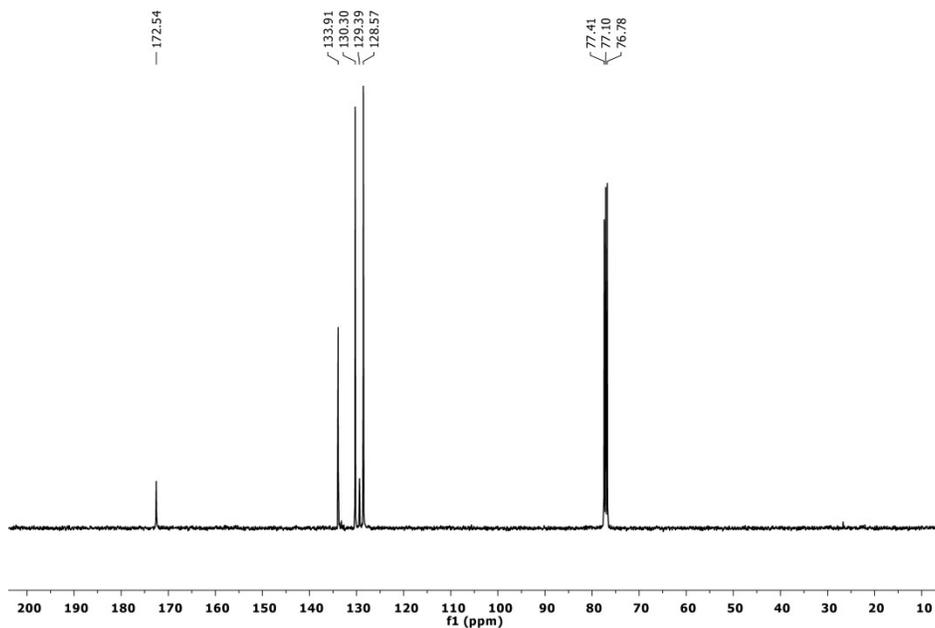


Figure S13. ^{13}C NMR (100 MHz, CDCl_3) of benzoic acid.

23. ESI-MS of products

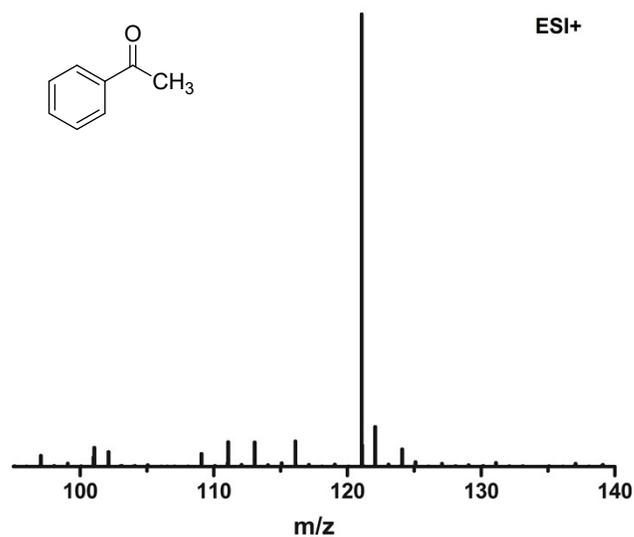


Figure S14. ESI-MS for molecular ion at $m/z = 121.08$ ($z = 1$) corresponds to $[M+H]^+$ where $M = C_8H_8O$.

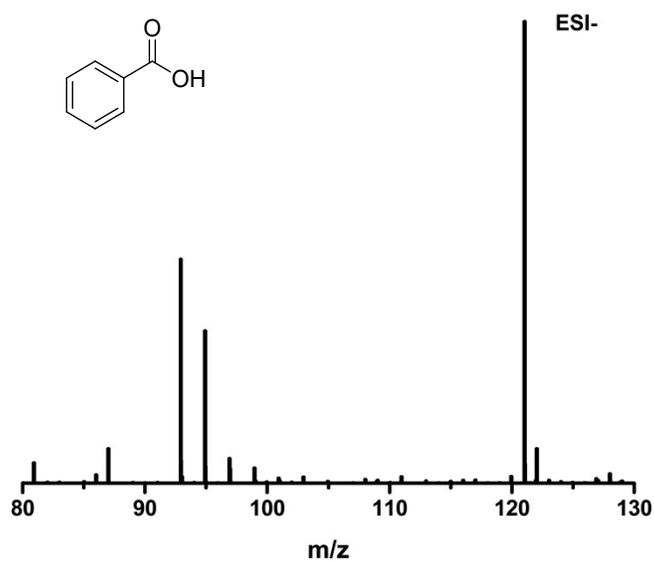


Figure S15. ESI-MS for molecular ion at $m/z = 121.02$ ($z = 1$) corresponds to $[M-H]^-$ where $M = C_7H_5O_2$.

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