

Supplementary Information

Aerobic Oxidation of Alkylarenes and Polystyrene Wastes to Benzoic Acids via Copper-based Catalyst

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Table of Contents

1.	General Information	3
2.	Procedure for the photooxidative reaction of alkylarenes.....	3
3.	Procedure for the degradation of PS wastes	5
4.	Mechanistic Studies.....	10
5.	Procedure for PS degradation on gram scale	13
6.	References	14

1. General Information

General: All reagents were used as received unless otherwise noted. CuCl_2 was purchased from Energy Chemical. CaCl_2 powder was purchased from Beijing Chemical Works. The methanol and MeCN were purchased from Sigma-Aldrich. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV); column chromatography purifications were carried out using silica gel. The reaction mixture was analyzed by using Waters High Performance Liquid Chromatograph (HPLC) system equipped with autosampler, C18 column (Length: 150 mm, Internal diameter: 4.6 mm, 35°C) and UV/Vis detector ($\lambda = 220 \text{ nm}$). CH_3OH : 0.1% HCOOH in H_2O was used as a mobile phase with a flow rate of 1.0 mL/min. ^1H NMR spectra was recorded at Bruker Avance II 500 (500 MHz, ^1H) instrument at room temperature (rt). Chemical shifts (δ) were reported as parts per million (ppm). Polystyrene number-average molecular weight (M_n) and molecular weight distributions ($\text{PDI} = M_w/M_n$) were measured by gel permeation chromatography (GPC) at 40°C and a flow rate of 1 mL/min, with THF (HPLC grade) as an eluent on a Waters 1515 instrument equipped with Waters $4.6 \times 30 \text{ mm}$ guard column and three Waters WAT054466, WAT044226, WAT044223 columns. The instrument was calibrated with PS standards, and chromatograms were processed with Waters Breeze2 software.

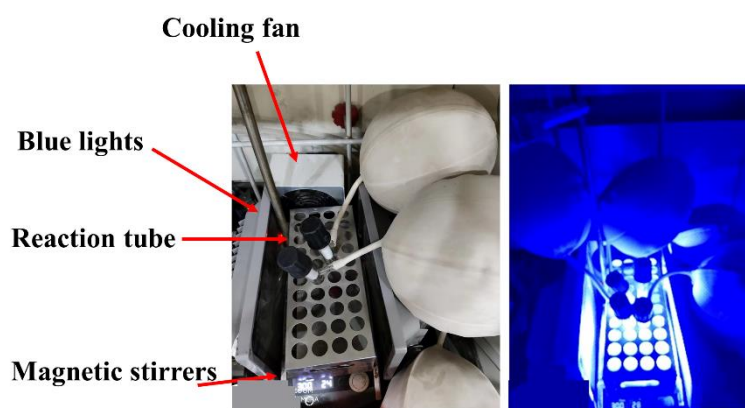
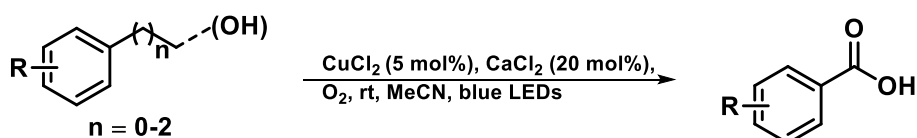


Figure S1. Reaction equipment setup (left) and during reaction (right).

2. Procedure for the photooxidative reaction of alkylarenes

2.1 General procedure for photooxidative cleavage of alkylarenes via CuCl_2



A 10 mL Schlenk tube with screw-cap was charged with substrate (0.1 mmol, 1 eq.), CuCl_2 (5 mol%, 0.67 mg), CaCl_2 (20 mol%, 2.2 mg) and 1.0 mL MeCN. An oxygen balloon was equipped to keep the oxygen atmosphere and the whole reaction tube was kept for 24-72 h under the irradiation of two Kessil H150B 50 W blue LEDs lamps at room temperature, by using a fan to control the temperature. After the reaction, the resulting mixture was dissolved with MeOH to constant volume in a 10 mL volumetric flask and then filtered. The filtrate was measured by HPLC equipped with autosampler.

2.2 HPLC analysis

The yields of products were measured without internal standard by HPLC equipped with autosampler using standard curve of standard substances as reference (All the standard curves have a linear relationship of $R^2 = 0.999$). Typical standard curves and chromatograms are shown as below:

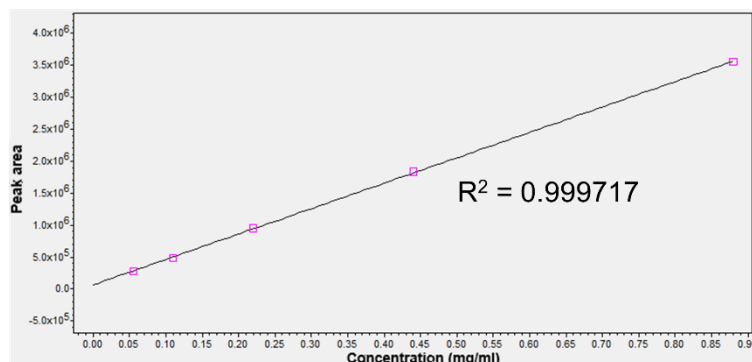
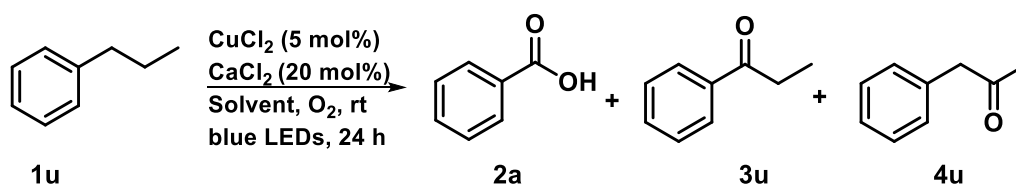


Figure S2. Typical HPLC standard curve of benzoic acid (**2a**).

2.3 Reaction condition optimization for propylbenzene as substrate

Table S1. Screening the solvents for the photooxidative cleavage of propylbenzene catalyzed by CuCl_2 .^a

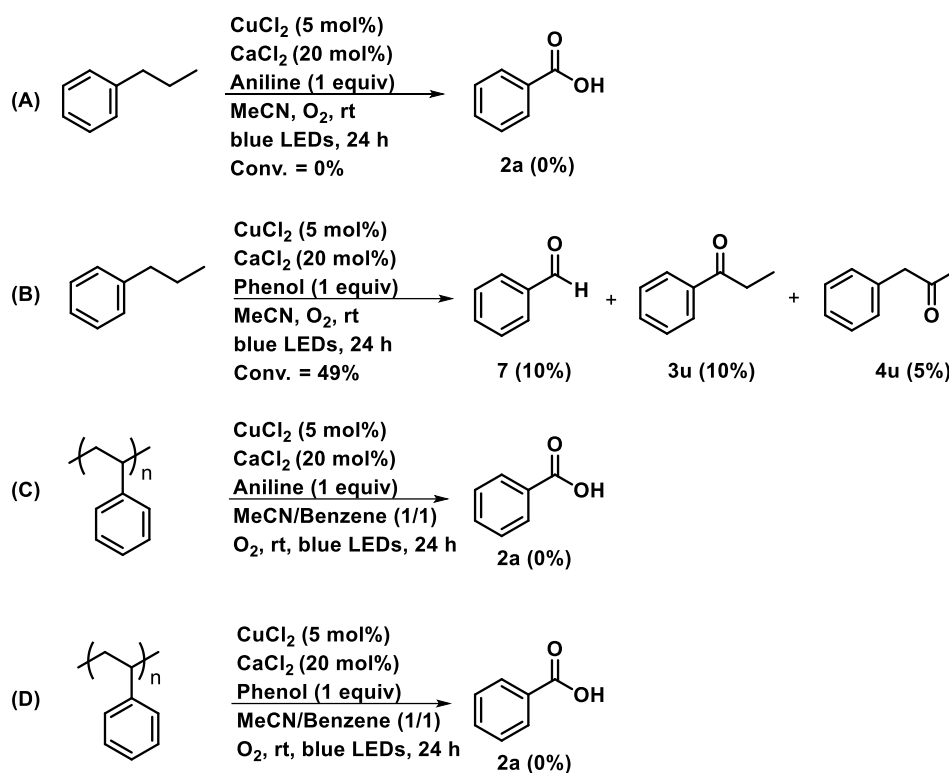


Entry	Solvent	Yield (%)		
		2a	3u	4u
1	MeCN	75	0	0
2	MeOH	0	4	0
3	THF	0	3	0
4	DCM	0	0	0
5	EtOAc	38	9	1
6	Acetone	21	2	0
7	DMF	7	2	2

^a Reaction condition: **1u** (0.1 mmol), CuCl_2 (5 mol%), CaCl_2 (20 mol%), 1.0 mL solvent, O_2 balloon, 50 W blue LEDs, rt, 24 h; the yields were measured by HPLC using standard curve of standards as reference.

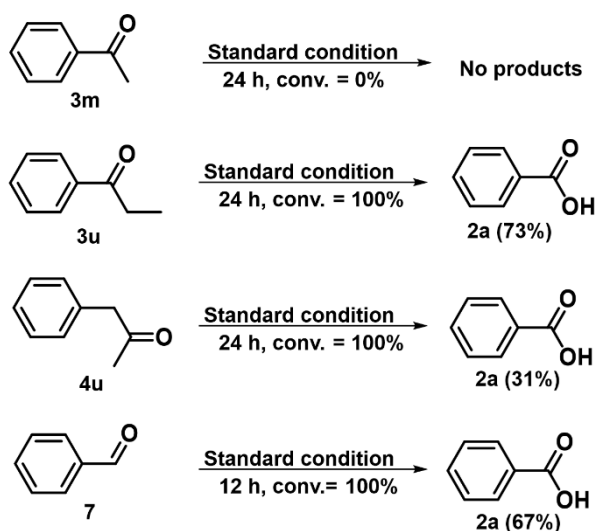
2.4 The experiment on functional group tolerance of aniline and phenol

Scheme S1. The reaction for the tolerance of aniline and phenol with the propylbenzene or polystyrene as substrates.



2.5 The reaction for ketone as substrates

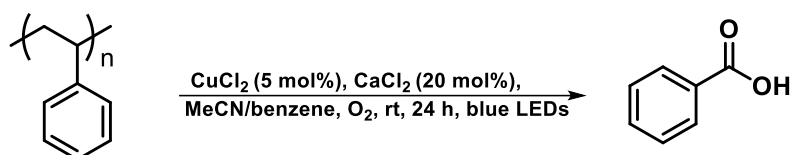
Scheme S2. The reaction for the ketone as substrates.



Standard condition: substrate (0.1 mmol), CuCl₂ (5 mol%), CaCl₂ (20 mol%), MeCN (1.0 mL), O₂ balloon, 50 W blue LEDs, rt; The conversion and yields were measured by HPLC using standard curve of standards as reference.

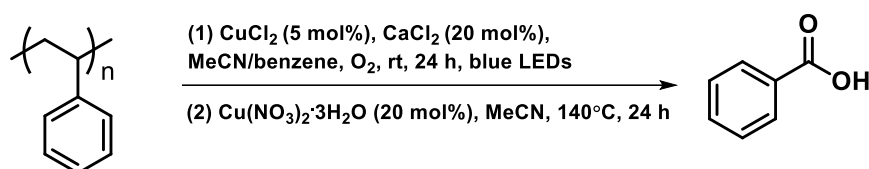
3. Procedure for the degradation of PS wastes

3.1 General procedure for the photooxidative degradation of PS via CuCl₂ catalyst



A 10 mL Schlenk tube with screw-cap was charged with polystyrene wastes (0.1 mmol, 10.4 mg), CuCl₂ (5 mol%, 0.67 mg), CaCl₂ (20 mol%, 2.2 mg) and MeCN/Benzene (0.3 mL/0.3 mL). The reaction mixture was stirred for 5 min in the dark. Then an oxygen balloon was equipped to keep the oxygen atmosphere and the whole reaction tube was kept for 24 h under the irradiation of two Kessil H150B 50 W blue LEDs lamps at room temperature, by using a fan to control the temperature. After reaction, the resulting mixture was dissolved with MeOH to constant volume in a 5 mL volumetric flask and then filtered with a PTFE syringe filter. The filtrate was measured by HPLC equipped with autosampler.

3.2 General one-pot two-step procedure for the oxidative degradation of PS



1st-step: A 10 mL Schlenk tube with screw-cap was charged with polystyrene wastes (0.1 mmol, 10.4 mg), CuCl₂ (5 mol%, 0.67 mg), CaCl₂ (20 mol%, 2.2 mg) and MeCN/benzene (0.3 mL/0.3 mL). The reaction mixture was stirred for 5 min in the dark. Then an oxygen balloon was equipped to keep the oxygen atmosphere and the whole reaction tube was kept for 24 h under the irradiation of two Kessil H150B 50 W blue LEDs lamps at room temperature, by using a fan to control the temperature.

2nd-step: After 1st-step, Cu(NO₃)₂·3H₂O (20 mol%, 4.8 mg), MeCN (1 mL) were added into the mixture of 1st-step, and then the mixture was degassed and exchanged with O₂. Next, the mixture was sealed in the pressure tube and heated at 140°C for 24 h, and then cooled down to room temperature after reaction. The resulting mixture was dissolved with MeOH to constant volume in a 5 mL volumetric flask and then filtered with a PTFE syringe filter. The filtrate was measured by HPLC equipped with autosampler.

3.3 Calculation Method for Products from Polystyrene Degradation

The yield of benzoic acid was measured by HPLC equipped with autosampler. The standard curve of benzoic acid is shown in Figure S2. The calculating equation for the yield of benzoic acid obtained from polystyrene degradation was listed as following:

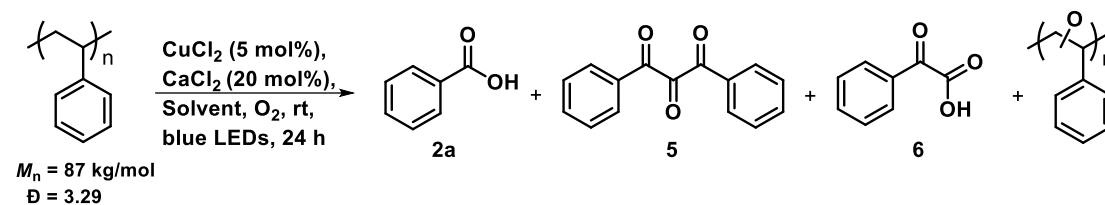
$$\text{Yield (\%)} = \frac{n_{\text{benzoic acid}}}{n_{\text{polystyrene}}} \times 100\%$$

$$n_{\text{polystyrene}} = \frac{\text{weight of polystyrene}}{M_w \text{ of styrene monomer (104 g/mol)}}$$

($n_{\text{benzoic acid}}$: moles of the benzoic acid; $n_{\text{polystyrene}}$: moles of the polystyrene; M_w : molecular weight of styrene monomer)

3.4 Reaction condition optimization for polystyrene as substrate

Table S2. Optimization study for the photooxidation degradation of polystyrene ^a



Entry	Solvent	M_n (kg/mol)	PDI (Đ)	Yield (%)		
				2a	5	6
1	MeCN	34	2.99	0	0	0
2	MeCN/benzene	0.11	3.81	22	3	6
3	MeCN/acetone	29	2.57	2	0	0
4	MeCN/THF	30	2.12	3	0	0
5	MeCN/EtOAc	26	1.59	3	0	0
6	MeCN/DCM	1.0	1.06	0	0	0

Reaction condition: commercial polystyrene (0.1 mmol, based on the mole amount of the styrene monomer), CuCl_2 (5 mol %), CaCl_2 (20 mol %), solvent (1/1, 0.6 mL), O_2 balloon, 50 W blue LEDs, rt, 24 h; The yields were measured by HPLC using standard curve of standards as reference.

3.5 The characterization of reaction mixture after degradation of polystyrene

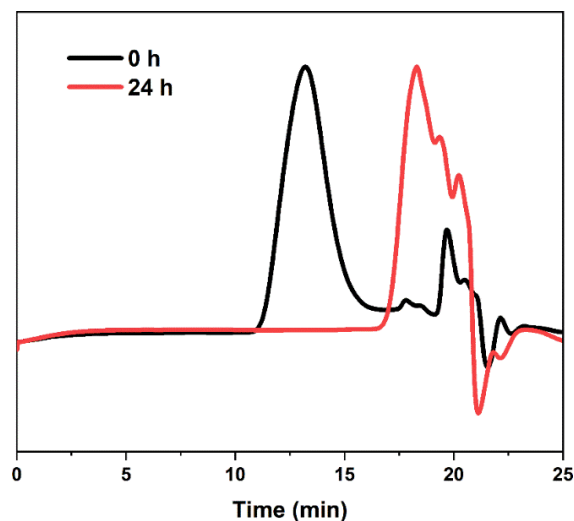


Figure S3. GPC traces obtained for polystyrene before and after 24 h of degradation.

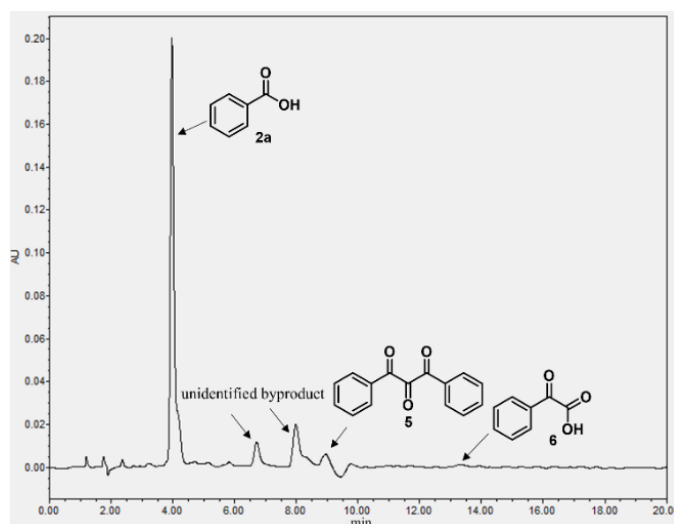


Figure S4. HPLC spectrum obtained after the PS photooxidative degradation via CuCl_2 under reaction condition for Scheme 3.

3.6 The effect of polystyrene additives on the degradation of polystyrene

The widely used polystyrene additives, such as antioxidants (e.g.: 2,6-di-tert-butyl-*p*-cresol (BHT) and propyl gallate), ultraviolet absorbers (e.g.: phenyl salicylate, 2-(2-hydroxy-5-methylphenyl)benzotriazole) and 2,4-dihydroxybenzophenone, foaming agents (e.g.: azodicarbonamide, 2,2-azobis(2-methylpropionitrile) and diethyl azodicarboxylate), were typically added in a range of 0.1-5 wt%. The medium amount (0.5 wt%) and maximum amount (5 wt%) of polystyrene additives were utilized to test the tolerance of our degradation system. The results were summarized in Table S3 and Table S4.

Common polystyrene additives:

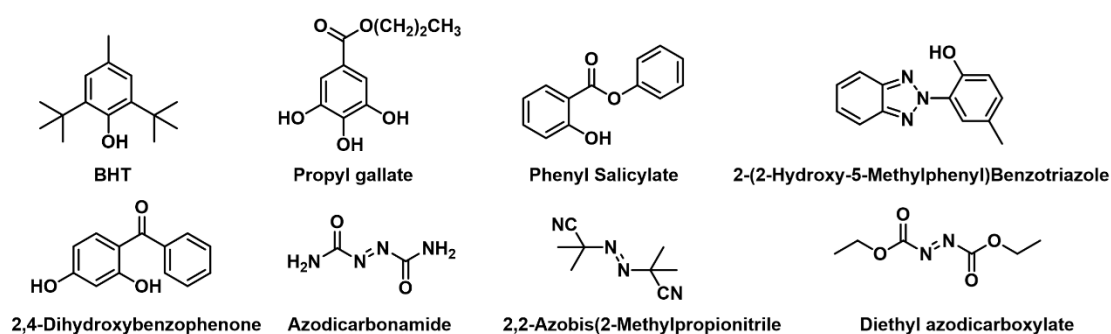
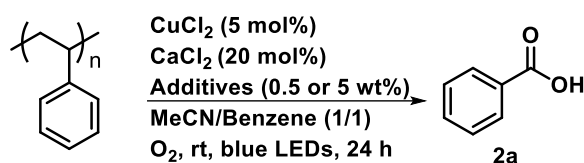


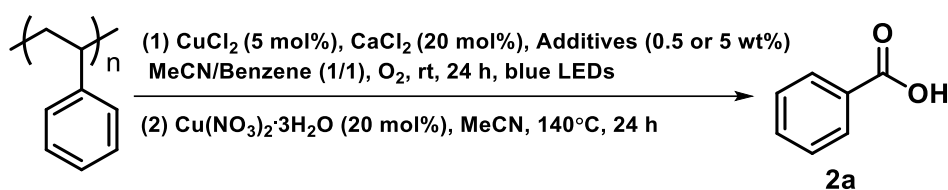
Table S3. The effects of polystyrene additives on the photooxidative degradation of polystyrene ^a



Entry	Additives		Yield of 2a (%)	
			0.5 wt%	5 wt%
1	---		22	22
2	Antioxidant	BHT	20 (0 ^b)	18
3		propyl gallate	20	19
4	Ultraviolet absorbent	phenyl salicylate	21	19
5		2-(2-hydroxy-5-methylphenyl)benzotriazole	19	18
6		2,4-dihydroxybenzophenone	24	20
7	azodicarbonamide		23	20
8	Foaming agent	2,2-azobis(2-methylpropionitrile)	22	20
9	diethyl azodicarboxylate		20	19

^a Reaction condition: pure polystyrene (90 kg/mol, 0.1 mmol, based on the mole amount of the styrene monomer), CuCl₂ (5 mol %), CaCl₂ (20 mol %), additives (0.5 or 5 wt%), MeCN/Benzene (0.6 mL), O₂ balloon, 50 W blue LEDs, rt, 24 h; The yields were measured by HPLC using standard curve of standard substances as reference. The average values were obtained from the HPLC yields of two parallel PS degradation experiments. ^b BHT (2 equiv).

Table S4. The effects of polystyrene additives on the oxidative degradation of polystyrene via one-pot two-step ^a

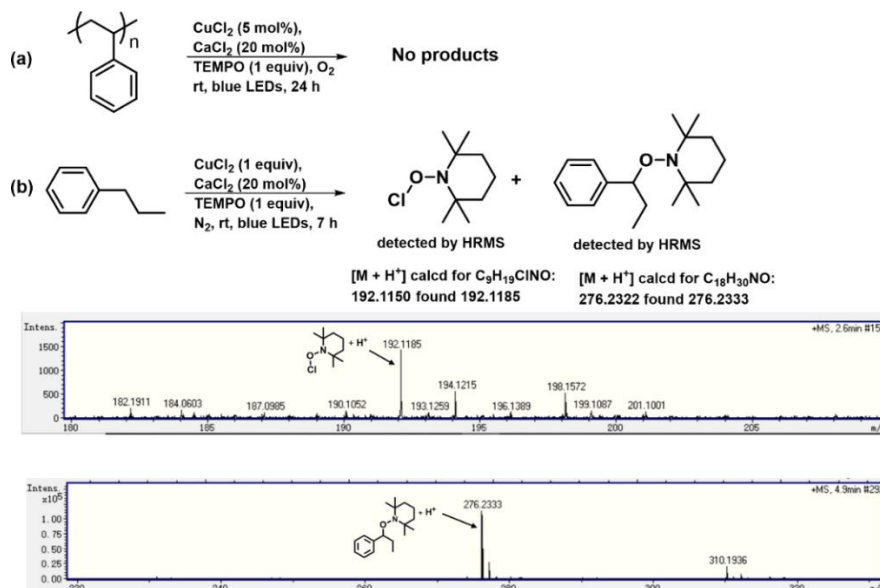


Entry	Additives		Yield of 2a (%)	
			0.5 wt%	5 wt%
1	---		53	53
2	Antioxidant	BHT	47 (0 ^b)	42
3		propyl gallate	48	46
4	Ultraviolet absorbent	phenyl salicylate	51	38
5		2-(2-hydroxy-5-methylphenyl)benzotriazole	52	26
6		2,4-dihydroxybenzophenone	51	45
7	azodicarbonamide		50	46
8	Foaming agent	2,2-azobis(2-methylpropionitrile)	47	39
9	diethyl azodicarboxylate		49	46

^a Reaction condition: 1st-step: pure PS (0.1 mmol, based on the mole amount of the styrene monomer), CuCl₂ (5 mol%), CaCl₂ (20 mol%), additives (0.5 or 5 wt%), MeCN/Benzene (0.6 mL), O₂ balloon, 50 W blue LEDs, rt, 24 h. 2nd-step: Cu(NO₃)₂·3H₂O (20 mol%), MeCN (1 mL) was added to the mixture obtained after 1st-step, 140°C, 24 h. The average values were obtained from the HPLC yields of two parallel PS degradation experiments. ^b BHT (2 equiv).

4. Mechanistic Studies

4.1 The radical intermediate trapping experiments



Scheme S3. (a) Using TEMPO as radical scavenger for the photocatalytic reaction of PS; (b) high-resolution mass spectra obtained for the photocatalytic reaction of propylbenzene by using TEMPO.

4.2 UV-vis absorption spectroscopy of $CuCl_2$

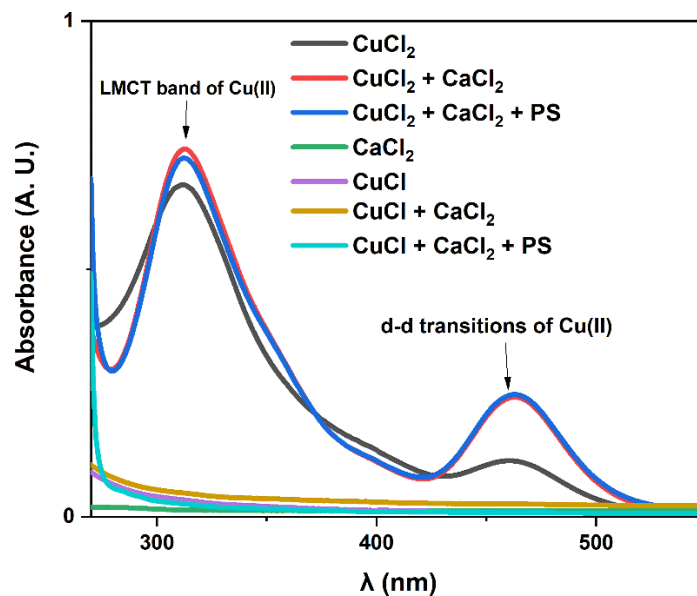


Figure S5. UV-vis absorption spectroscopy of $CuCl_2$ related reaction components in MeCN/Benzene.

4.3 The time-dependent GPC traces

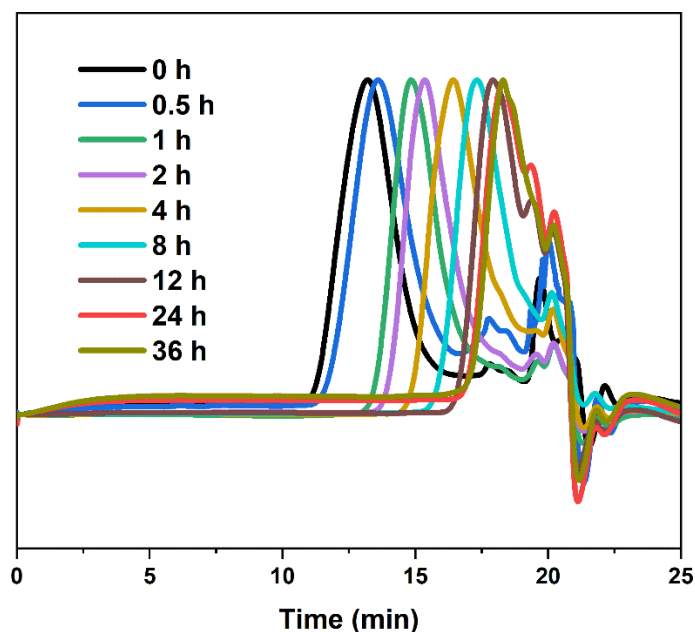


Figure S6. The time-dependent GPC traces obtained for photocatalytic oxidative degradation of polystyrene.

4.4 The time-evolution experiments for photocatalytic degradation of PS with different M_n

To gain deeper insight into the effects of number-average molecular weight (M_n) of polystyrene on the radical reactivity, we monitored the yields of benzoic acid (**2a**) for the degradation of PS with different M_n (Figure S7). There is no **2a** detected in the first 4 h. From 4 to 20 h, the formation rate of **2a** for low M_n was slightly faster than that for higher M_n . The yields of **2a** reached 20% around for both polystyrenes in 24 h.

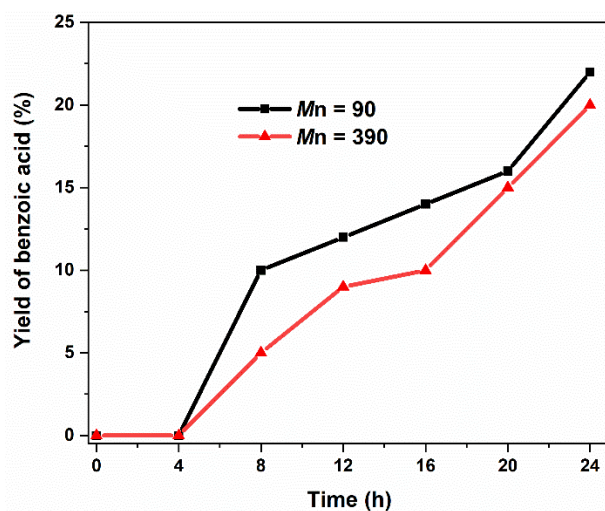


Figure S7. Effects of different M_n of polystyrene on the photooxidative degradation of PS catalyzed by CuCl_2 .

4.5 Mechanistic reaction of small molecular substrates

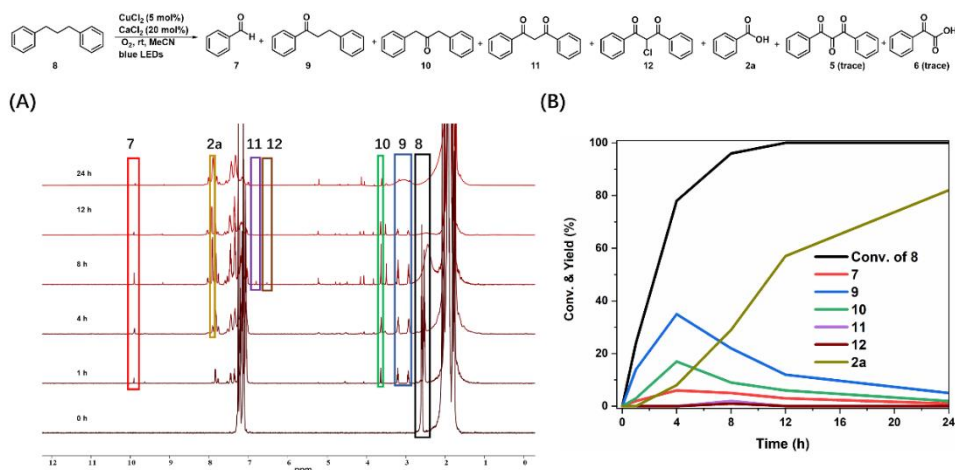


Figure S8. The time-dependent ¹H NMR spectra obtained for reaction of 1,3-diphenylpropane (**8**). Reaction condition: **8** (0.1 mmol), CuCl₂ (5 mol%), CaCl₂ (20 mol%), MeCN (1.0 mL), O₂ balloon, blue LEDs, rt.

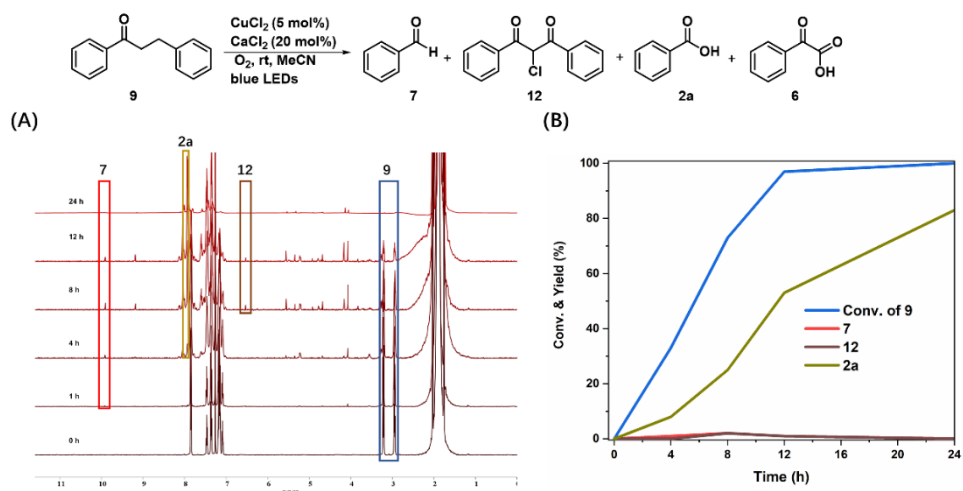


Figure S9. The time-dependent ¹H NMR spectra obtained for reaction of 1,3-diphenylpropan-1-one (**9**). Reaction condition: **9** (0.1 mmol), CuCl₂ (5 mol%), CaCl₂ (20 mol%), MeCN (1.0 mL), O₂ balloon, blue LEDs, rt.

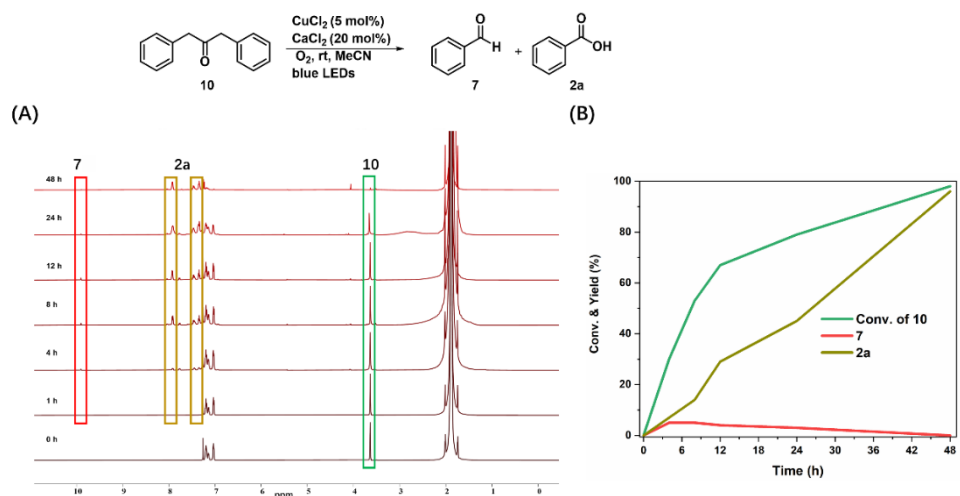


Figure S10. The time-dependent ¹H NMR spectra obtained for reaction of 1,3-diphenylpropan-2-one (**10**). Reaction condition: **10** (0.1 mmol), CuCl₂ (5 mol%), CaCl₂ (20 mol%), MeCN (1.0 mL), O₂ balloon, blue LEDs, rt.

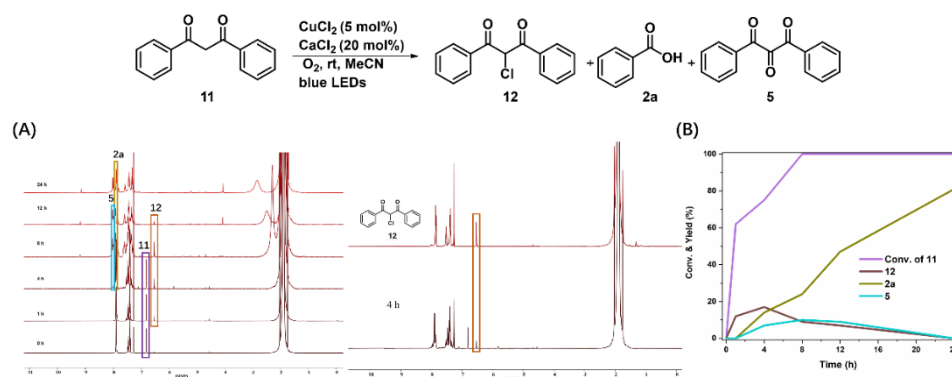


Figure S11. The time-dependent ¹H NMR spectra obtained for reaction of 1,3-diphenylpropane-1,3-dione (**11**). Reaction condition: **11** (0.1 mmol), CuCl₂ (5 mol%), CaCl₂ (20 mol%), MeCN (1.0 mL), O₂ balloon, blue LEDs, rt.

5. Procedure for PS degradation on gram scale

1st-step: A 250 mL Schlenk tube with screw-cap was charged with PS foam (10 mmol, 1.04 g), CuCl₂ (5 mol%, 67 mg), CaCl₂ (20 mol%, 222 mg), MeCN/Benzene (30 mL/30 mL). The reaction mixture was stirred for 5 min in the dark. Then an oxygen balloon was equipped to keep the oxygen atmosphere and the whole reaction tube was kept for 72 h under the irradiation of two Kessil H150B 50 W blue LEDs at room temperature, by using a fan to control the temperature. (Note: illumination time is based on a constant amount of produced benzoic acid). 2nd-step: The Cu(NO₃)₂·3H₂O (20 mol%, 483 mg), MeCN (10 mL) were added into the mixture of 1st-step, and then the mixture was degassed and exchanged with O₂. Next, the mixture was sealed in the pressure tube and heated at 140°C for 24 h, and then cooled down to room temperature after reaction completion. HPLC analysis revealed that benzoic acid was produced in 50% yield (The average values were obtained from the HPLC yields of two parallel PS degradation experiments). The benzoic acid was obtained via following procedure:¹ Firstly, the resulting solution was concentrated to a solid under vacuum, and then dissolved with CH₂Cl₂ (20 mL). Next, the pH of organic solution was adjusted to 10 by using aqueous solution of NaOH (0.5 M) and stirred for 10 min. The aqueous phase was separated and collected via a separatory funnel. Meanwhile, the organic phase was further washed with 0.5 M NaOH aqueous solution (20 mL × 2), and aqueous phases were collected. Then, the combined aqueous phase was adjusted to pH = 2 with 2 M HCl and then stirred for 10 min. After that, the resulting acidic solution was extracted with CH₂Cl₂ (20 mL × 3), and the combined organic phase was dried over Na₂SO₄, and concentrated under reduced pressure to afford the crude benzoic acid product in 0.57 g without further purification (The average values were obtained from the HPLC yields of two parallel PS degradation experiments; Figure S12).

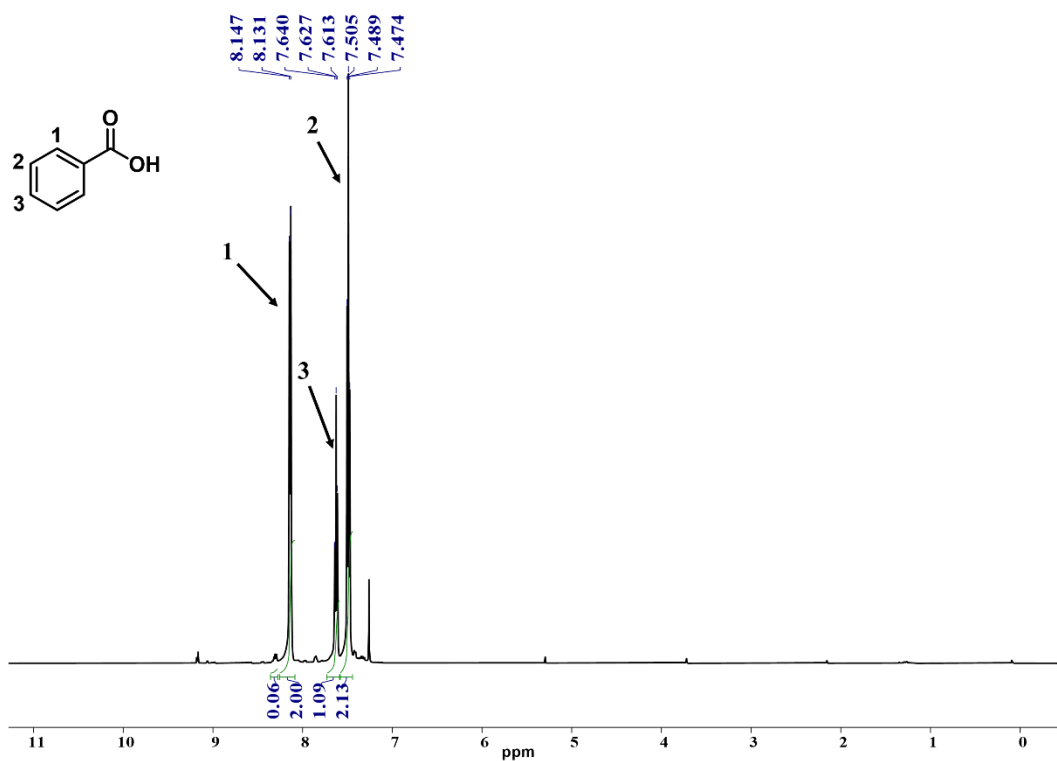


Figure S12. The ¹H NMR spectrum of the crude benzoic acid.

6. References

- 1 a) Y. Qin, T. Zhang, H. Y. V. Ching, G. S. Raman and S. Das, *Chem*, 2022, 8, 2472-2484; b) N. F. Nikitas, E. Skolia, P. L. Gkizis, I. Triandafillidi and C. G. Kokotos, *Green Chem.*, 2023, 25, 4750-4759.