Supporting Information

Experimental procedure

All the reagents were commercially available and used without further purifications. For the synthesis of $ZnIn_2S_4$, $ZnCl_2$ (0.136 g, 1 mmol), $InCl_3 \cdot 4H_2O$ (0.586 g, 2 mmol) and thioacetamide (TAA) (0.3 g, 4 mmol) were added in a mixed solution containing 30 mL of N,N-dimethylformamide (DMF) and 30 mL of ethylene glycol (EG) under vigorous stirring. The resultant suspension was transferred to a 100 mL Teflon liner, sealed and heated at 180 °C for 18 h. After the reaction, the autoclave was cooled, and the product was collected and washed with deionized water and ethanol for several times and dried at 60 °C for 12 h.

Catalytic reactions

The oxidative cleavage reactions of olefins were carried out in a sealed reaction tube irradiated with an LED lamp (Beijing Perfect Light, PCX50B). The catalyst (10 mg), benzyl mercaptane (0.1 mmol) and olefins (0.1 mmol) were suspended in a Schlenk tube containing acetonitrile (CH_3CN, 4 ml), with the reaction vial open to air. The reaction was performed under irradiation for 15 h with an LED lamp (65 mW cm^{-2}) irradiated from bottom, with the reaction suspension continuously stirring during the whole reaction. The mixture was filtered through a porous membrane (20 μm in diameter) and the filtrate was analyzed by GC-MS and GC-FID (Shimadzu GC-2014) equipped with an HP-5 capillary column.

To obtain the AQE of the photocatalytic oxidative cleavage of styrene over $ZnIn_2S_4$ at 420, 460 and 500 nm, the reaction system was irradiated by a LED lamp with a bandpass filter which centered at 420, 460 and 500 nm, respectively. The AQE was calculated based on the following equation:

$$AQE\ (\%) = \frac{n \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100$$

n: Number of electrons transferred by reaction

M: The amount of product

S: Light receiving area

P: Light intensity

t: Reaction time

λ: Incident light wavelength

N_A: Avogadro constant, h: Planck constant, c: Speed of light.

Detection of the intermediate dioxetane

The catalyst $ZnIn_2S_4$ (10 mg), benzyl mercaptane (0.1 mmol), styrene (0.1 mmol) and L-methionine (0.2 mmol) were suspended in a Schlenk tube containing CH_3CN (3.5 ml) and H_2O (0.5 ml), with the reaction vial open to air. The reaction was performed under irradiation for 15 h with an LED lamp (65 mW cm^{-2}) irradiated from bottom, with the reaction suspension continuously stirring during the whole reaction. Analysis by GC-MS showed the formation of 1-phenyl-1,2-ethanediol. MS (EI): fragmentation pattern was in accord with the one in database for 1-phenyl-1,2-ethanediol.

Characterizations

The X-ray diffraction (XRD) patterns of the resultant products were collected on a MiniFlex600 X-ray diffractometer (Rigaku, Japan) using Cu Kα (λ = 1.5406 Å) radiation. The accelerating voltage and the applied current were 40 kV and 15 mA, respectively. XRD patterns were scanned over the angular range of 5-90° (2θ) with a step size of 0.02°. The morphology of the samples was examined by field emission scanning electron microscopy (SEM) (JSM-6700F). UV-visible diffuse reflectance spectra (UV-vis DRS) of the powders were obtained for the dry-pressed disk samples using a UV-vis spectrophotometer (Cary 500 Scan Spectrophotometers, Varian, USA). $BaSO_4$ was used as a reflectance standard. BET surface area measurements were carried out on an ASAP 2020M apparatus (Micromeritics Instrument Corp., USA). The samples were degassed in vacuum at 150 ^{o}C for 10 h and then measured at −196 ^{o}C. The ESR spectra were determined on a Bruker A300 ESR spectrometer.

Figure S1 XRD pattern of $ZnIn_2S_4$
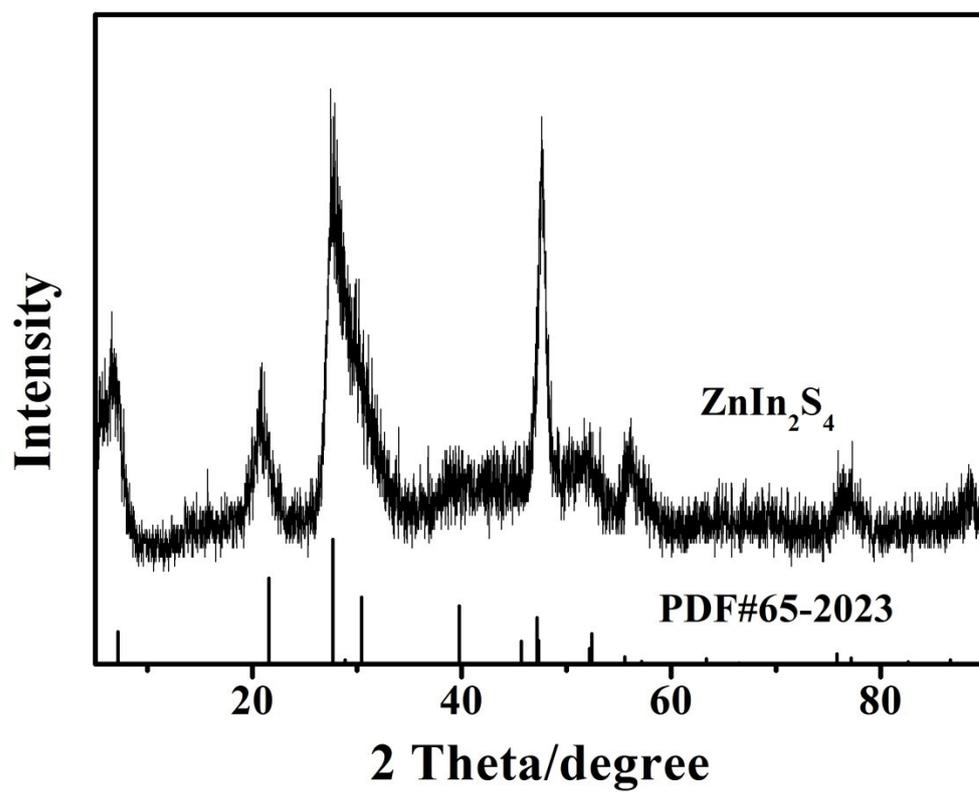
Figure S2 SEM image of ZnIn$_2$S$_4$
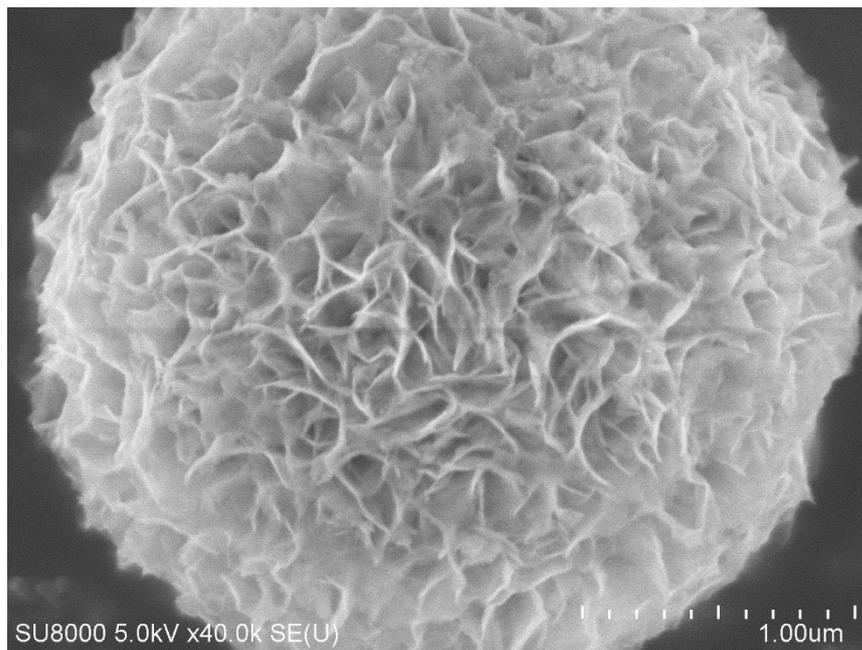
Figure S3 Nitrogen adsorption−desorption isotherms of $ZnIn_2S_4$. Inset: Pore size distribution curve of the as-prepared samples calculated from desorption branch of the nitrogen isotherm by the BJH method
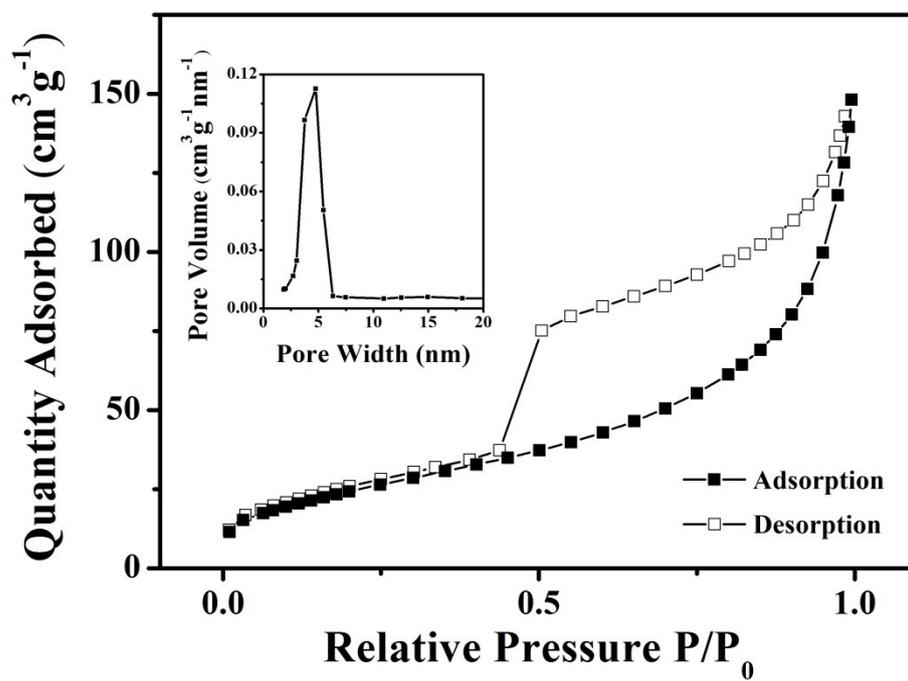
Figure S4 UV-Vis diffuse reflectance spectra of ZnIn$_2$S$_4$
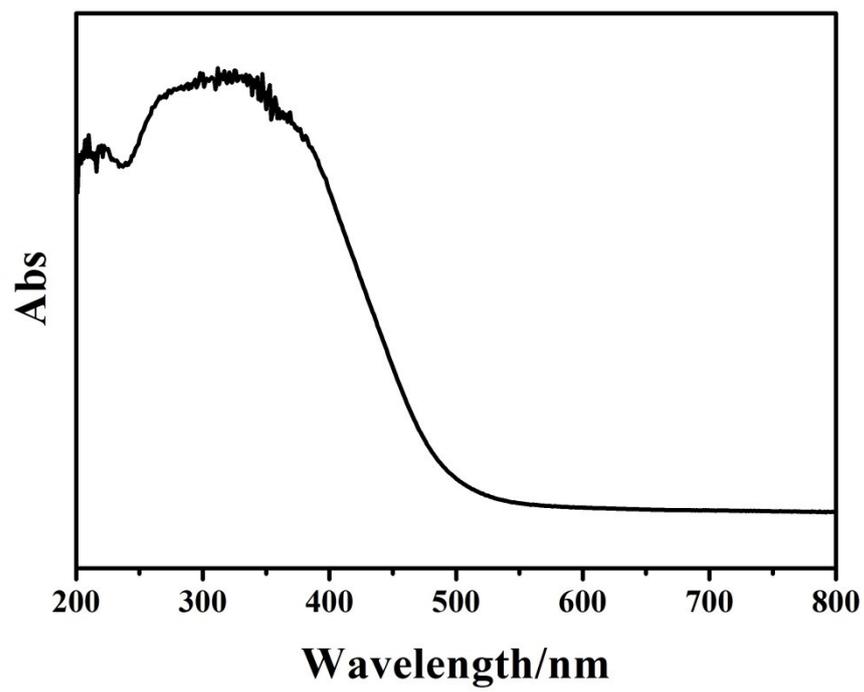
Figure S5 (a) The AQE of the photocatalytic oxidative cleavage of styrene at 420 nm, 460 nm and 500 nm; (b) UV-vis DRS of $ZnIn_2S_4$.
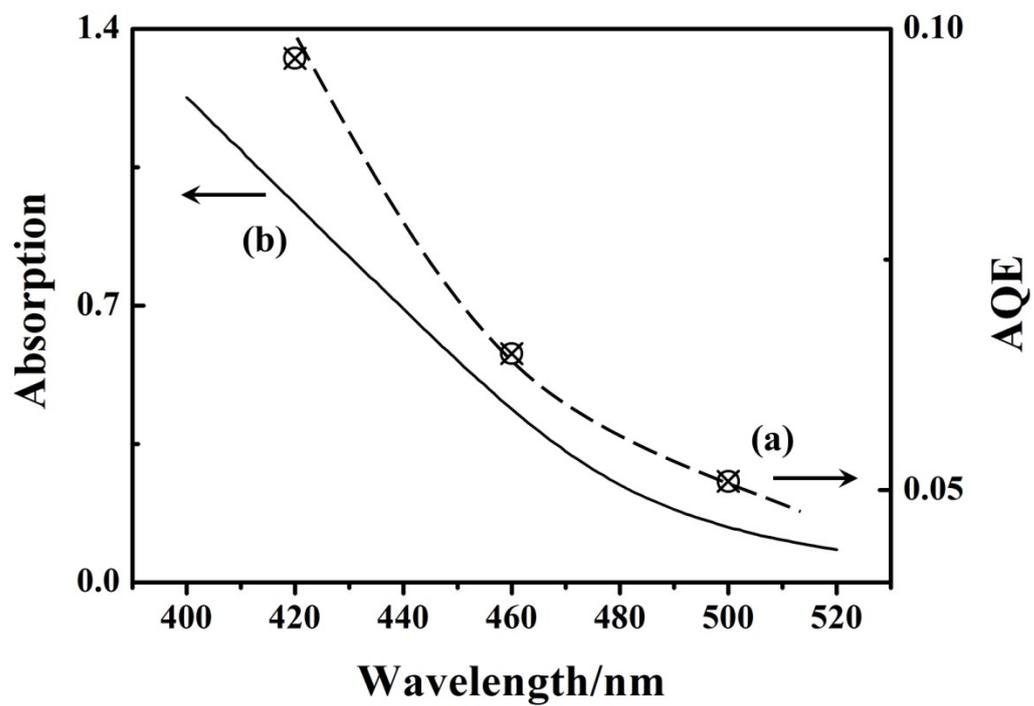
Figure S6 GC-MS signals of the intermediate dioxetane trapped by methionine
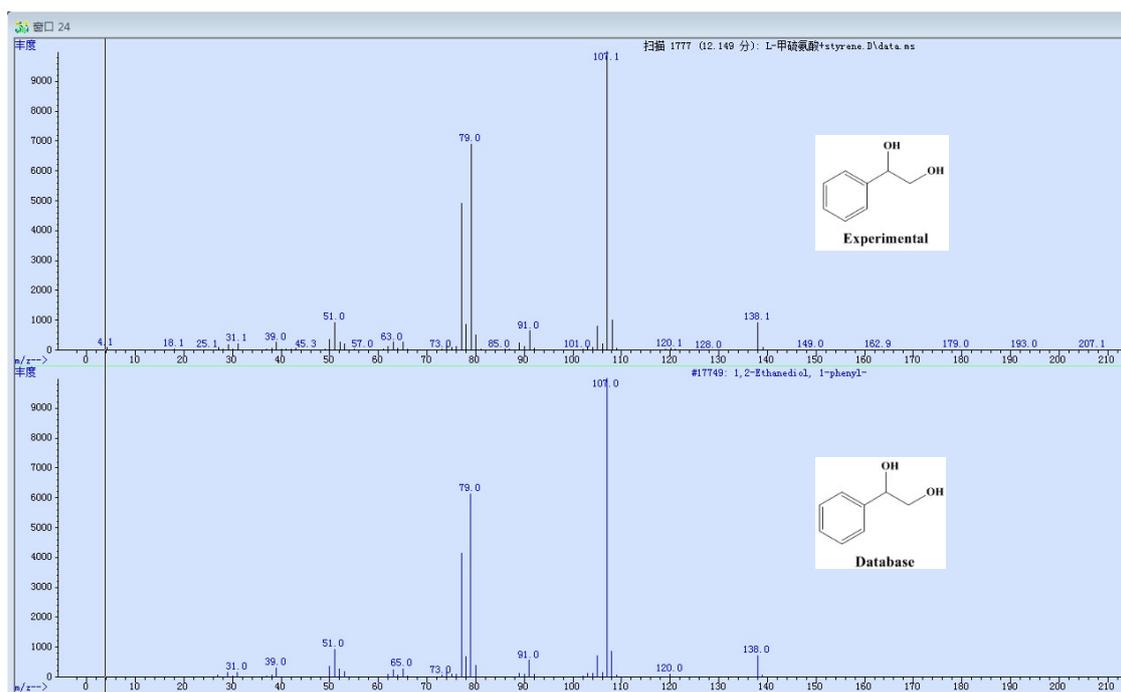
Figure S7 Cycling of $ZnIn_2S_4$ for the oxidative cleavage of olefins in the presence of benzyl mercaptane under visible-light irradiation
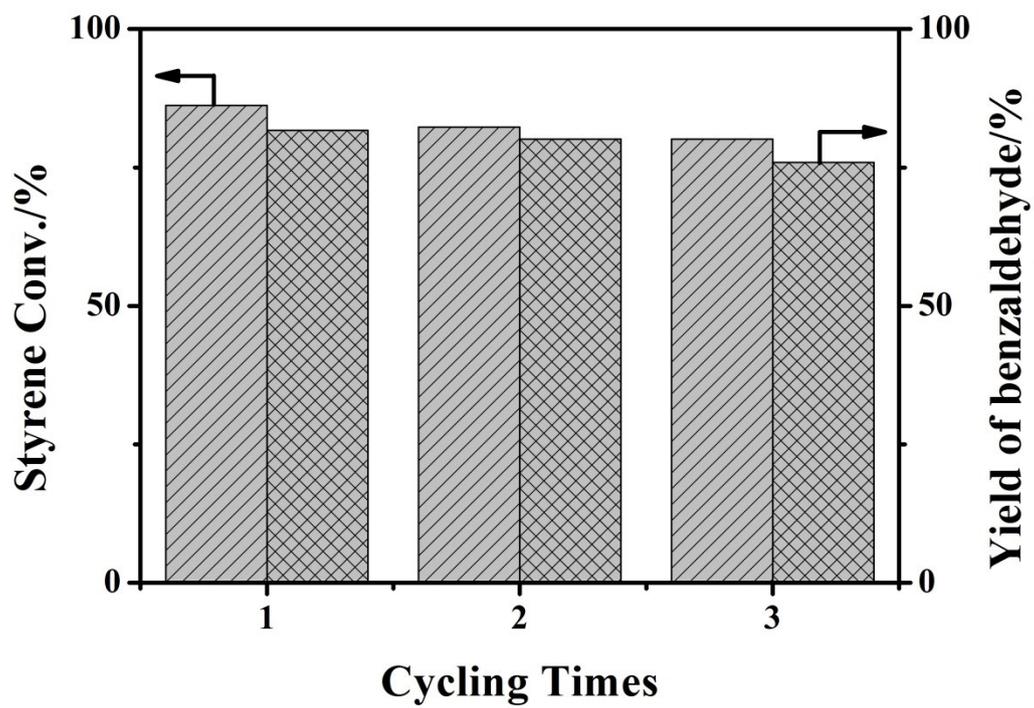
Figure S8 XRD diffraction patterns of (a) fresh $ZnIn_2S_4$ and (b) used $ZnIn_2S_4$ (after three cycling reactions for the oxidative cleavage of olefins in the presence of benzyl mercaptane)
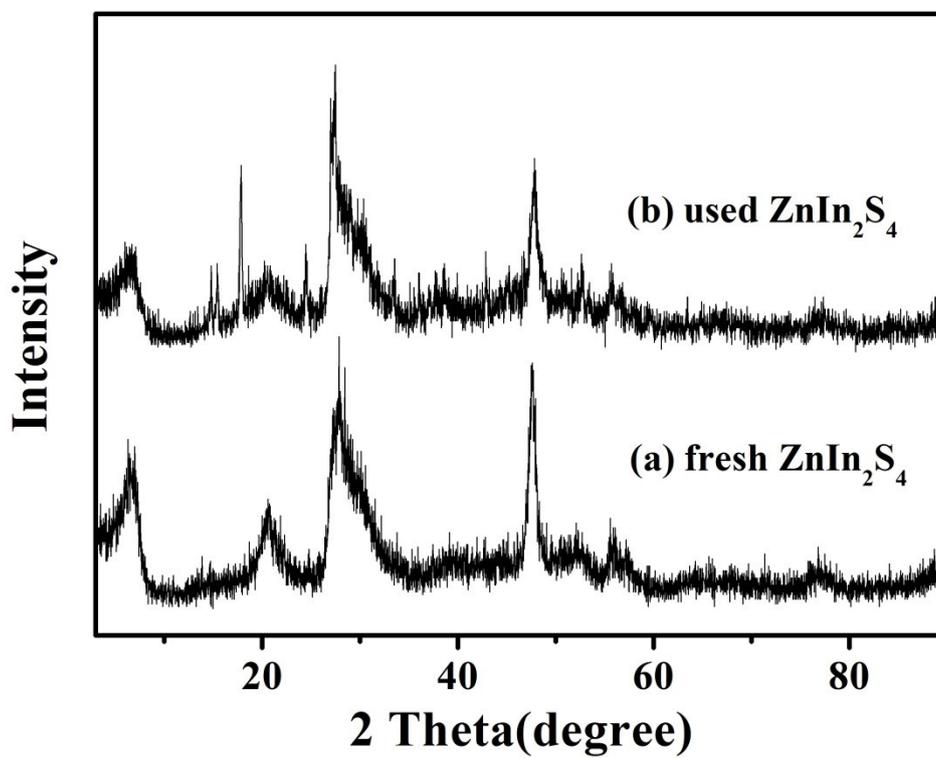
Table S1 Controlled experiments carried out in the presence of either DMPO or benzoquinone
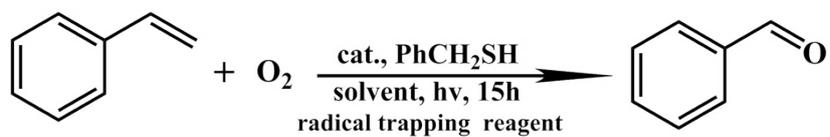
Entry	Radical trapping (0.2 mmol)	Styrene/ Conv.	Benzaldehyde/ Yield
1	-	81%	78%
2	DMPO	5%	-
3	Benzoquinone	7%	-

Conditions: styrene (0.1 mmol), benzyl mercaptane (0.1 mmol), $ZnIn_2S_4$ (10 mg), CH_3CN (4 mL), under air, visible light irradiation for 15 h.