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Thiols Initiated Photocatalytic Oxidative Cleavage of C=C Bond in Olefins and its Extension to Direct Production of Acetals from Olefins

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Abstract

The oxidative cleavage of olefins to produce aldehydes/ketones is an important reaction in organic syntheses. In this manuscript, a mild and operationally simple protocol for the aerobic oxidation of olefins to produce carbonyl compounds was realized over $ZnIn_2S_4$ under visible light, using air as the oxidant and the thiol as the initiator. It was proposed that the photo-generated holes over $ZnIn_2S_4$ attack the thiol to produce thiyl radicals, which initiate the oxidative cleavage of the C=C bond in olefins to produce aldehydes/ketones. By further coupling with the condensation between the as-obtained aldehydes/ketones and alcohols, this strategy can also be applied to the production of different acetals directly from the olefins. This study demonstrates a new pathway in realization of the oxidative cleavage of olefins to produce aldehydes/ketones, and also provides a new protocol for the production of acetals directly from the olefins.

Keywords: olefin, oxidative cleavage, thiyl radicals, aldehydes/ketones, acetal, photocatalysis

Introduction

The oxidative cleavage of olefins to produce aldehydes/ketones is an important reaction in organic syntheses since it can use inexpensive olefin feedstocks to produce organic compounds with carbonyl functional groups.[1,2] Although traditional methods including ozonolysis or using the Lemieux-Johnson Protocol, ie, OsO_4 followed by $NaIO_4$,[3,4] have been used for the oxygenation of olefins, the related safety concern limits their applications. Alternatively, metal-free reactions using equivalent oxidants like *m*-chloroperbenzoic acid (*m*CPBA) and the developed aryl-λ^3-iodane,[5] or the combination of transition metal-based catalysts with peroxides, peracids and other oxidizing reagents,[6-8] have also been applied for the C=C bond cleavage. However, the use of either over-stoichiometric amounts of oxidants or the expensive metals not only produces a large amount of by-products, but also increases the processing cost.

Abundant molecular O_2 is considered to be an ideal oxidant in oxygenation reactions due to its inexpensive and environmentally friendly characteristics.[9] As an economically attractive protocol to introduce oxygen-containing functional groups into the organics, oxidation reactions based on different catalytic systems using O_2 as the oxidants is in particular attractive for large scale applications.[10,11] Actually, oxidative cleavage of olefins to produce aldehydes/ketones using O_2 as the oxidant has also been demonstrated over a variety of catalytic systems.[12-15] For example, Kroutil *et al.* described a simple bio-catalytic alkene cleavage to yield aldehydes.[16] Catalyzed by $Pd(OAc)_2$ in the presence of pressured O_2 under an elevated temperature, a wide range of olefins were oxidative cleaved, via the formation of 1,2-diols or dioxo-Pd^{II} complexes as the precursors to the final carbonyl compounds.[17] Alternatively, oxidative cleavage of olefins to aldehydes/ketones can also be realized via the radical pathways.[18-21] For example, thermal activation of *Tert*-butyl nitrite (TBN) under a metal free condition was found to release alkoxyl radicals, which served as initiators to induce selective C=C cleavage to produce aldehydes/ketones.[18] N-hydroxyphthalimide (NHPI) also served as a metal-free catalyst for the oxidative cleavage of C=C bonds. Thermal hemolysis of NHPI led to the formation of PINO radicals, which attacked the C=C double bond to produce carbon radicals and further trapped by molecular O_2 to give peroxyl radicals.[19] However, these oxygenation reactions have to be carried out under high temperature to activate either the substrates or the catalysts, and in some cases, high pressured oxygen is also required.

As compared with the traditional thermal activated processes, light initiated reactions can be carried out in a mild condition and therefore can be more selective since some undesirable thermally induced side reactions can be inhibited.[22-25] Since most of the organic compounds are only responsive in the UV light region, the initial studies in this field were carried out under UV irradiations.[26] For example, the UV light irradiations on CBr_4 led to the formation of Br radicals, which initiate the aerobic photo-oxidative cleavage of the C=C bond of α- or β-substituted styrenes.[27] However, the possible decomposition of the involved reactive peroxides under UV irradiations lowered the yields to the desirable aldehydes/ketones.[28] By formation of a visible light responsive charge transfer (CT) complexes between oxygen and the olefins inside the cages of the zeolites, Frei and coworkers reported the visible light induced oxygenations of 2,3-dimethyl-2-butene via dioxetanes as the intermediate.[29] Singlet oxygen ($^1O_2$) generated by visible light irradiations on a platinum(II) polypyridyl complex has also been reported to oxidative cleavage of the C=C bonds.[30] Recently, Wang and coworkers reported an interesting protocol to realize the aerobic oxidative cleavage of C=C bonds to produce aldehydes/ketones under visible light, using electron-rich aromatic disulfides as the photocatalyst.[31] Both experimental and computational studies suggest that a disulfide-olefin charge-transfer complex formed is responsible for the facile dissociation of disulfide S-S bond under visible light to generate thiyl radicals, which attack the C=C bonds to form the carbon-centered radicals and further trapped by O_2 to afford aldehyde/ketone via dioxetane as the intermediates.

Considering that thiyl radicals can initiate the oxidative cleavage of C=C bonds to produce aldehydes/ketones, and stimulated by our previous studies that thiyl radicals can be generated when $ZnIn_2S_4$ was irradiated under visible light in the presence of the thiols,[32,33] herein we investigated the oxygenation of alkenes over irradiated $ZnIn_2S_4$ with the presence of thiols. Ternary $ZnIn_2S_4$ is a ternary chalcogenide with a band gap well responsive in the visible-light region, which has been widely studied for photocatalytic H_2 evolution and light induced organic syntheses.[34-41] A successful oxidative cleavage of a variety of olefins to produce aldehydes/ketones was found to be realized over visible light irradiated $ZnIn_2S_4$, with benzyl mercaptane as the additive. Our system is the first demonstration that such a reaction can be realized over a visible light induced semiconductor-based photocatalyst, using thiol as an initiator. In addition, the current photocatalytic system can also be applied to the one-pot syntheses of different acetals from the reaction between the olefins and alcohols in the presence of the thiol (benzyl mercaptane).

Results and discussion

$ZnIn_2S_4$ was prepared through a solvothermal method from $ZnCl_2$, $InCl_3$ and thioacetamide (TAA) in a mixture of ethylene glycol (EG) and N,N-dimethylformamide (DMF). The XRD diffraction patterns of the product are indexed to hexagonal $ZnIn_2S_4$ (JCPDS 65-2023) (Supporting Figure S1).[42] The SEM image shows that the product is composed of flowerlike microspheres with a dimension of approximately 1 μm, which is made up of numerous interwoven nanoflakes (Supporting Figure S2). The N_2 adsorption/desorption isotherms of the as-obtained $ZnIn_2S_4$ were also studied, with its BET specific surface area determined to be 91.32 m^2/g (Supporting Figure S3). The UV-Vis diffuse reflectance spectrum (UV-vis DRS) of the product shows that it has strong absorption in the visible light region, with an absorption edge extending to ca. 490 nm, corresponding to a band gap of ca. 2.5 eV (Supporting Figure S4).

To study the performance of $ZnIn_2S_4$ for the oxidative cleavage of olefins to form aldehydes/ketones, styrene was first chosen as the substrate and the reaction was initially carried out in dichloromethane (CH_2Cl_2), in the presence of equimolar of benzyl mercaptane (to styrene) under visible light, using air as the oxidant. It was found that 28.1% of styrene was converted after irradiated for 15h, with a yield of 23% to benzaldehyde, the oxidative product (Table 1, entry 1). To study the influence of the solvent, the reaction carried out in anisole, paraxylene, cyclohexane, methylbenzene and acetonitrile (CH_3CN) was also investigated. It was found that for these solvents, a conversion of styrene ranged from 25.7 to 81.2% and a yield to the desired benzaldehyde ranged from 14.5 to 77.9% was realized (Table 1, entries 2-6). Among all the solvents investigated, CH_3CN was found to be the best one for this reaction, by showing the highest styrene conversion ratio of 81.2% and an optimum yield of 77.9% to benzaldehyde after irradiated for 15 h. In the meantime, 84.5% of benzyl mercaptane was converted, yielding disulfide (58.2%) and benzylsulfonic acid (19.1%).[43] The time-dependent conversion of styrene and the formation of benzaldehyde was investigated and the result was shown in Fig. 1. Obviously the conversion of the substrate (styrene) and the yield to the desired product (benzaldehyde) increases with the irradiation time. No conversion of styrene was observed either in absence of $ZnIn_2S_4$ or in dark (Table 1, entries 7 and 8). The AQE of the photocatalytic oxidative cleavage of styrene at 420 nm, 460 nm and 500 nm was determined to be 0.097, 0.068 and 0.051 respectively. The AQE depends on the wavelength in a manner that correlates with the absorption intensities of $ZnIn_2S_4$ in the visible light region (Supporting Figure S5), indicating that it is truly a photocatalytic reaction. In addition, almost negligible styrene was converted in absence of benzyl mercaptane under otherwise similar conditions (Table 1, entry 9), indicating that benzyl mercaptane is essential for the oxidative cleavage of styrene to produce benzaldehyde. The amount of the benzyl mercaptane also influenced the performance. The yield to benzaldehyde decreased from 77.9% to 32.0% when only 0.02 equimolar of benzyl mercaptane (to styrene) was used in the reaction (Table 1, entry 10). On the contrary, a slightly increased yield to benzaldehyde (82.5%) was observed when the amount of benzyl mercaptane was increased to 2 equimolar (to styrene) (Table 1, entry 12).

The above results clearly indicate that benzyl mercaptane is involved in the oxidative cleavage of C=C bond in styrene to produce benzaldehyde over irradiated $ZnIn_2S_4$. Our previous studies revealed that the hydrothiolation reactions between thiols and unsaturated alkenes/alkynes can be realized over visible light irradiated $ZnIn_2S_4$, in which the photogenerated holes in $ZnIn_2S_4$ attack the thiols to produce the thiyl radicals and initiate the thio-ene/yne reactions.[33] Similarly, photo-generated holes in $ZnIn_2S_4$ can also attack the benzyl mercaptane to produce the thiyl radicals, which is supposed to initiate the oxidative cleavage of C=C bond in styrene. To confirm this assumption, the ESR of the reaction system, a suspension containing $ZnIn_2S_4$, styrene, benzyl mercaptane and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) in CH_3CN, was studied. The DMPO spin-trapping ESR spectra of the reaction system under visible light irradiation shows four typical signals corresponding to the DMPO-thiyl adducts, a confirmation of the generation of thiyl radicals under visible light (Fig. 2). In addition, control experiments were carried out in the presence of radical trapping agents including DMPO and benzoquinone (BQ). The introduction of either DMPO or BQ led to a significantly lower activity for the oxidative cleavage of styrene, with only 5% and 7% of styrene converted under otherwise similar conditions, for the system containing DMPO or BQ respectively (Supporting Table S1), confirming that the radicals did involve in the reaction. It is proposed that the thiyl radicals can attack the C=C bond in styrene to produce the carbon-centered radical **2** (step 2), which are further trapped by oxygen to form superoxide radical **3** (step 3). Key intermediate dioxetane **4** produced, which upon heterolysis, gives the final oxygenation products, with the concomitant release of the thiyl radicals to complete the catalytic cycle (step 4). The change of air to pure O_2 did not influence the conversion of styrene obviously (81.2% in air vs. 78.3% in O_2, entries 6 and 13), indicating that the trapping of the carbon-centered radical 2 by O_2 to form superoxide radical 3 is not the rate limiting step. However, when the intensity of the irradiation decreased from 65 mW /cm^2 to 32.5 mW /cm^2, the conversion of styrene decreased from the original 81.2% to 59.5% (Table 1, entries 6 and 14). As shown in Table 1 (entries 6, 10 and 11), the amount of the initiator added (benzyl mercaptane) also influenced the activity. Therefore, it is believed that the photo-generation of the thiyl radicals is the rate limiting step in this reaction. The mechanism for the formation of benzaldehyde from styrene over irradiated $ZnIn_2S_4$ in the presence of benzyl mercaptane was shown in Scheme 1.

It is obvious that the formation of benzaldehyde from styrene also follows a radical-mediated oxidative pathway, in which thiyl radicals attack the C=C bond in the presence of oxygen to form the dioxetane as the important intermediate, a pathway previous proposed for the oxidative cleavage of olefins to produce aldehydes/ketones,[44] except that the thiyl radicals in the current system are produced by the attack of photogenerated holes on the benzyl mercaptane. The proposed mechanism was also confirmed by the detection of 1-phenyl-1-methyl-1,2-ethanediol by GC-MS when methionine and water was introduced into the reaction system, since previous study has revealed that although the dioxetane, the important intermediate **4**, is not stable, it can be trapped by methionine and water to form the detectable diol (Supporting Figure S6).[45] A small amount of benzylsulfonic acid was also detected in the reaction system, which may be formed due to the oxidation of the thiyl radicals by O_2 (step 5). The presence of this side reaction lead to slightly lower amount of the photogenerated thiyl radicals and as a result, a slightly lowering of the activity was observed after three consecutive cycling reactions even though the photocatalyst was stable as evidenced from its similar XRD patterns (Supporting Figure S7 and S8). Surely the coupling of the thiyl radicals to produce disulfides also occurs (step 6). However, when irradiated, the disulfides will also be cleaved to regenerate the thiyl radicals for the reactions.

The photo-oxidative cleavage of olefins over visible light irradiated $ZnIn_2S_4$ using benzyl mercaptane as the initiator can also be applied to a wide scope of substrates (Table 2). Styrenes with different functional groups in the benzene ring, including both electron-withdrawing substituents (*p*-F, *p*-Cl and *o*-Cl) as well as electron-donating groups (*p*-OCH_3 and *p*-CH_3) can all be converted to their corresponding aldehydes in yields of 65.2-80.5% (Table 2, entries 1-5). No obvious electronic effect was observed in this reaction. In addition, the reactions using either α-methylstyrene or 1,1-diphenylethylene as the substrate led to the formation of acetophenone (81.2%) and benzophenone (73.4%), the ketone products (Table 2, entries 6,7).

Acetals are important intermediates in organic syntheses and found wide applications in chemical and medicinal industry.[46,47] Acetals are usually obtained from aldehydes/ketones. Considering that the oxidative cleavage of the olefins to produce aldehydes/ketones can be realized over the current catalytic system under visible light, it would be an ideal protocol to couple it with the condensation between aldehydes/ketones and alcohols to directly produce acetals from olefins. Therefore, the reactions between different olefins and several alcohols were investigated in the presence of benzyl mercaptane over visible light irradiated $ZnIn_2S_4$. To our expectation, all the investigated reactions occur smoothly, leading to corresponding acetals with yields ranged from 38% to 81% (Table 3). In addition, the photocatalytic system showed high stability during the reaction, as evidenced from the cycling reactions as well as its unchanged XRD patterns after the reaction (Fig. 3 and 4).

Conclusion

In summary, the oxidative cleavage of olefins to produce aldehydes/ketones was realized over $ZnIn_2S_4$ under visible light, using air as the oxidant and the benzyl mercaptane as the initiator. The holes photogenerated over $ZnIn_2S_4$ attack the thiols to produce thiyl radicals, which are added to the C=C bond in olefins and are oxidized to produce aldehydes/ketones. This strategy not only can be applied to a broad scope of olefins, but also can be coupled with the further condensation between the as-obtained aldehydes/ketones and alcohols to yield acetals directly from the olefins. This study demonstrates a new pathway in realization of the oxidative cleavage of olefins to produce aldehydes/ketones, and also provides a new protocol for the production of acetals directly from the olefins.

Acknowledgements

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Captions for Figures

Fig. 1 Time-dependent changes in the amounts of styrene and benzaldehyde under visible-light irradiation over $ZnIn_2S_4$

Fig. 2 DMPO spin-trapping ESR spectra of the reaction system containing $ZnIn_2S_4$, styrene, benzyl mercaptan and CH_3CN (a) in the dark and (b) under visible light irradiation

Fig. 3 Cycling of $ZnIn_2S_4$ for the reaction between styrene and methanol in the presence of benzyl mercaptane under visible-light irradiation

Fig. 4 XRD diffraction patterns of (a) fresh $ZnIn_2S_4$ and (b) used $ZnIn_2S_4$ (after three cycling reactions between styrene and methanol)

Captions for Tables

Table 1 Light induced catalytic performance for the oxidative cleavage of styrene in the presence of benzyl mercaptane over $ZnIn_2S_4$ under different conditions

Table 2 Investigations of the substrate scope of the oxidative cleavage of olefins in the presence of benzyl mercaptane over $ZnIn_2S_4$

Table 3 Light induced production of acetals from olefins in the presence of benzyl mercaptane over $ZnIn_2S_4$

Caption for Scheme

Scheme 1 Proposed mechanism for the oxidative cleavage of olefins in the presence of benzyl mercaptane over $ZnIn_2S_4$ under visible light

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Fig. 1

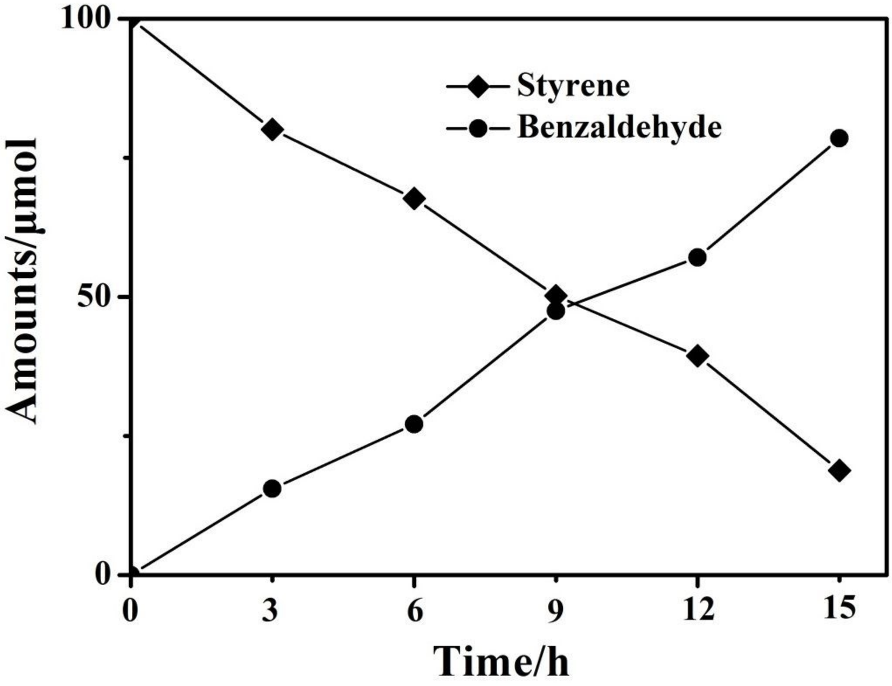

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Fig. 2

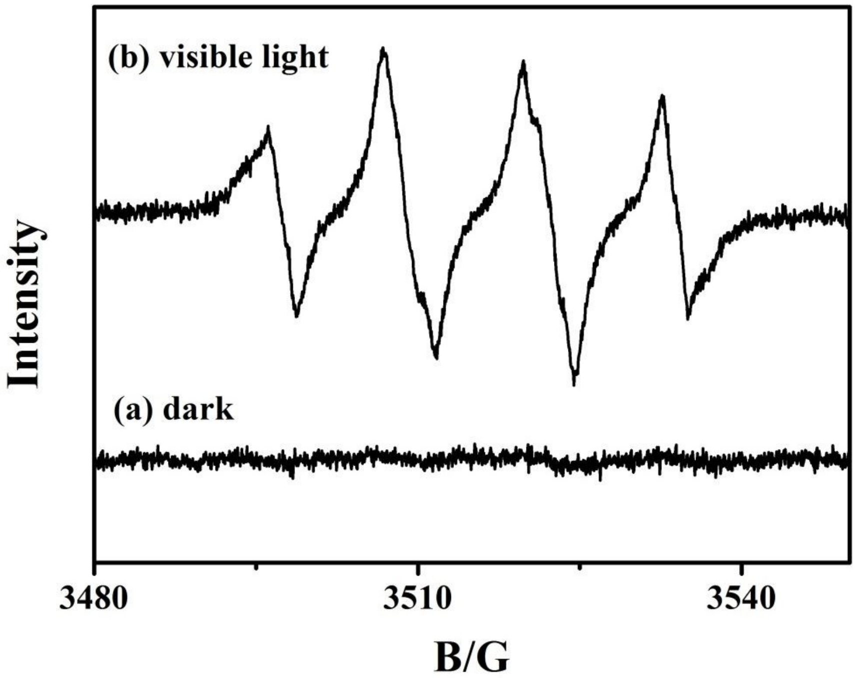

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Fig. 3

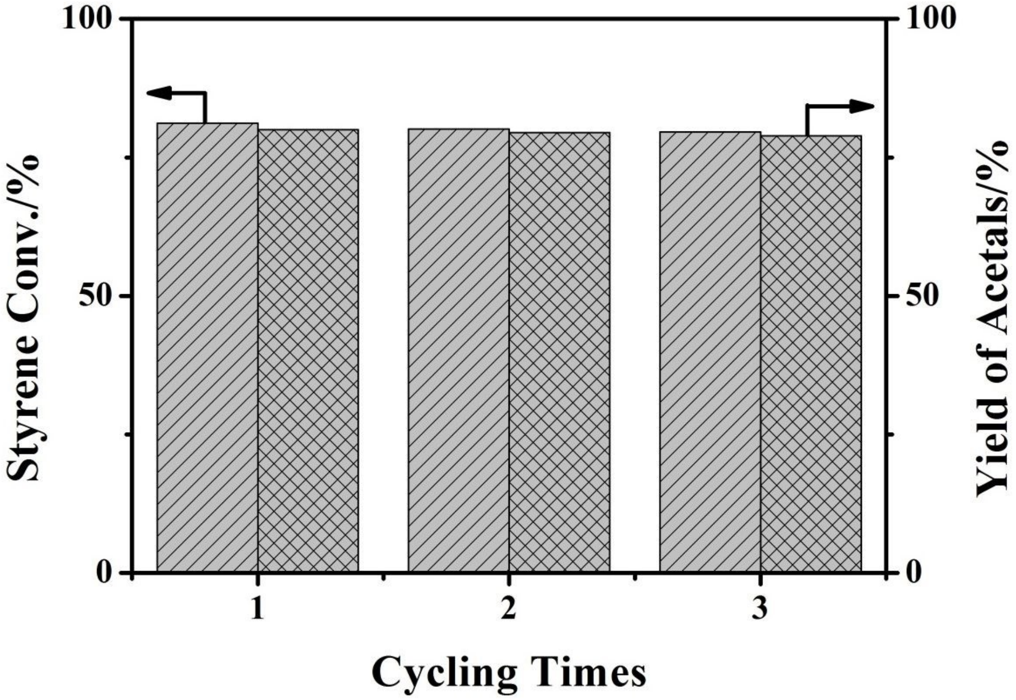

Fig. 4

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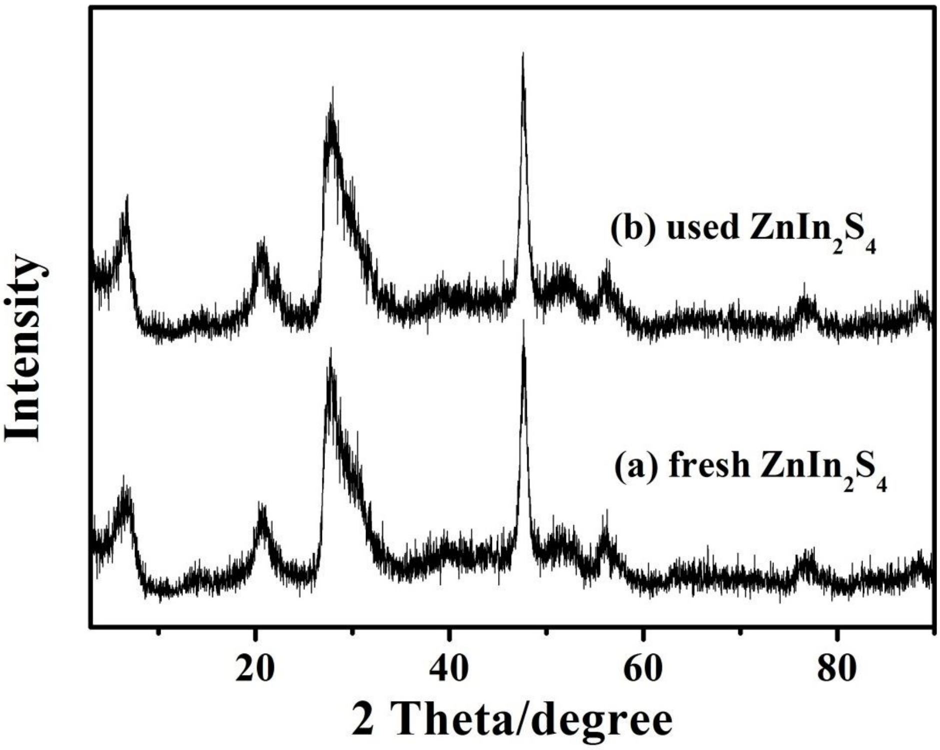

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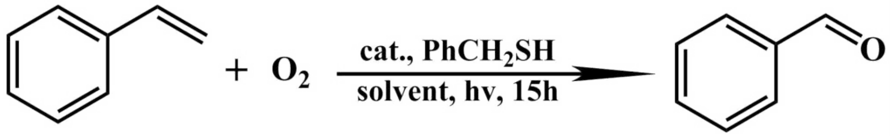
Table 1



Entry	$PhCH_2SH$ /mmol	Solvent	Styrene/ Conv.	Benzaldehyde/ Yield[e]
1	0.1	Dichloromethane	28.1%	23.0%
2	0.1	Anisole	25.7%	14.5%
3	0.1	Paraxylene	26.3%	23.5%
4	0.1	Cyclohexane	29.0%	24.6%
5	0.1	Methylbenzene	30.1%	27.8%
6	0.1	Acetonitrile	81.2%	77.9%
7[a]	0.1	Acetonitrile	-	-
8[b]	0.1	Acetonitrile	-	-
9[c]	0.1	Acetonitrile	-	-
10	0.02	Acetonitrile	46.1%	32.0%
11	0.06	Acetonitrile	55.2%	42.9%
12	0.2	Acetonitrile	88.6%	82.5%
13[d]	0.1	Acetonitrile	78.3%	75.1%
14[f]	0.1	Acetonitrile	59.5%	55.4%

Conditions: styrene (0.1 mmol), benzyl mercaptane, $ZnIn_2S_4$ (10 mg), solvent (4 mL), under air, visible light irradiation for 15 h. a. without $ZnIn_2S_4$; b. without light; c. without benzyl mercaptane; d.in pure O_2; f. irradiation for 15 h with lower light intensity (32.5 mW/cm^2); e. The amount of the products was calculated based on GC and GC-MS.

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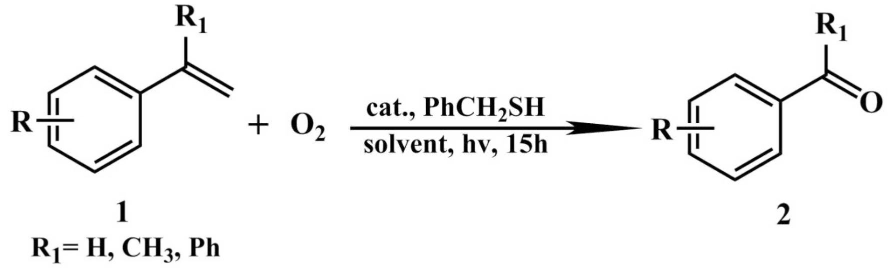
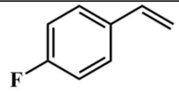
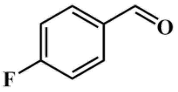
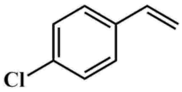
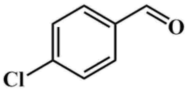
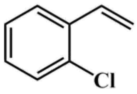
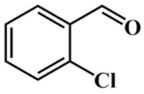
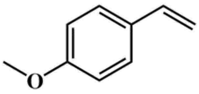
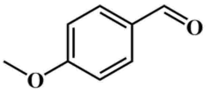
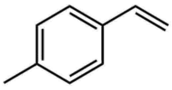
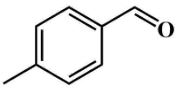
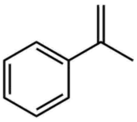
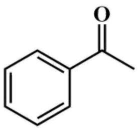
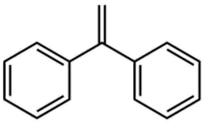
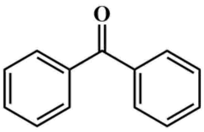
Table 2



Entry	Aromatic olefin (conv./%)	Products (yield/%)[a]
1	 **1a** (81.7)	 **2a** (75.7)
2	 **1b** (83.4)	 **2b** (79.8)
3	 **1c** (84.1)	 **2c** (80.5)
4	 **1d** (74.4)	 **2d** (66.1)
5	 **1e** (71.1)	 **2e** (65.2)
6	 **1f** (89.4)	 **2f** (81.2)
7	 **1g** (79.0)	 **2g** (73.4)

Conditions: Aromatic olefins (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; a. The amount of the products was calculated based on GC and GC-MS.

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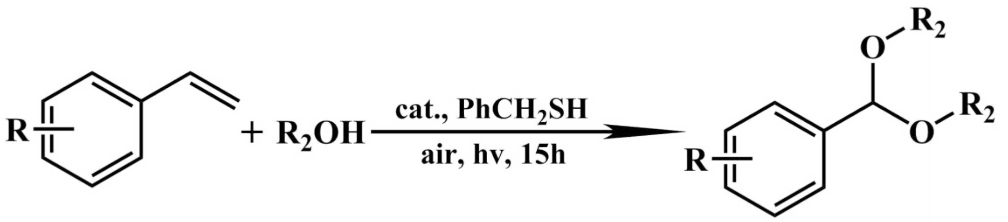
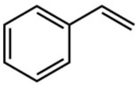
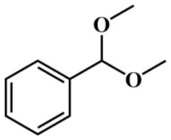
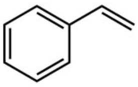
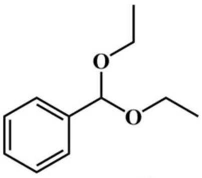
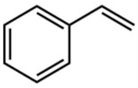
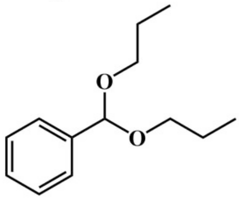
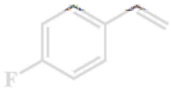
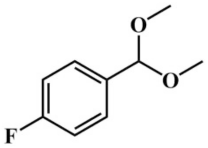
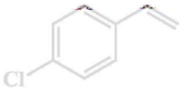
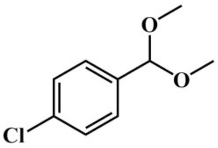
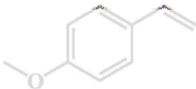
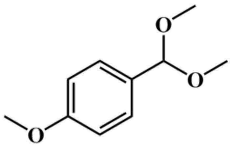
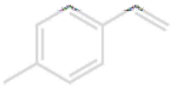
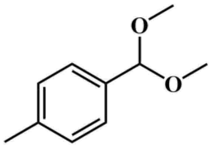
Table 3



Entry	Styrene	Alcohol	Aromatic acetals	Yield (%)$^{a, b}$
1		CH_3OH		81
2		C_2H_5OH		56
3		C_3H_7OH		38
4		CH_3OH		71
5		CH_3OH		78
6		CH_3OH		75
7		CH_3OH		70

Conditions: Aromatic olefins (0.1 mmol), benzyl mercaptane (0.1 mmol), $ZnIn_2S_4$ (10 mg), alcohols (4 mL), under air, visible light irradiation for 15h; a. conv. was calculated based on olefins; b. The amount of the products was calculated based on GC and GC-MS.

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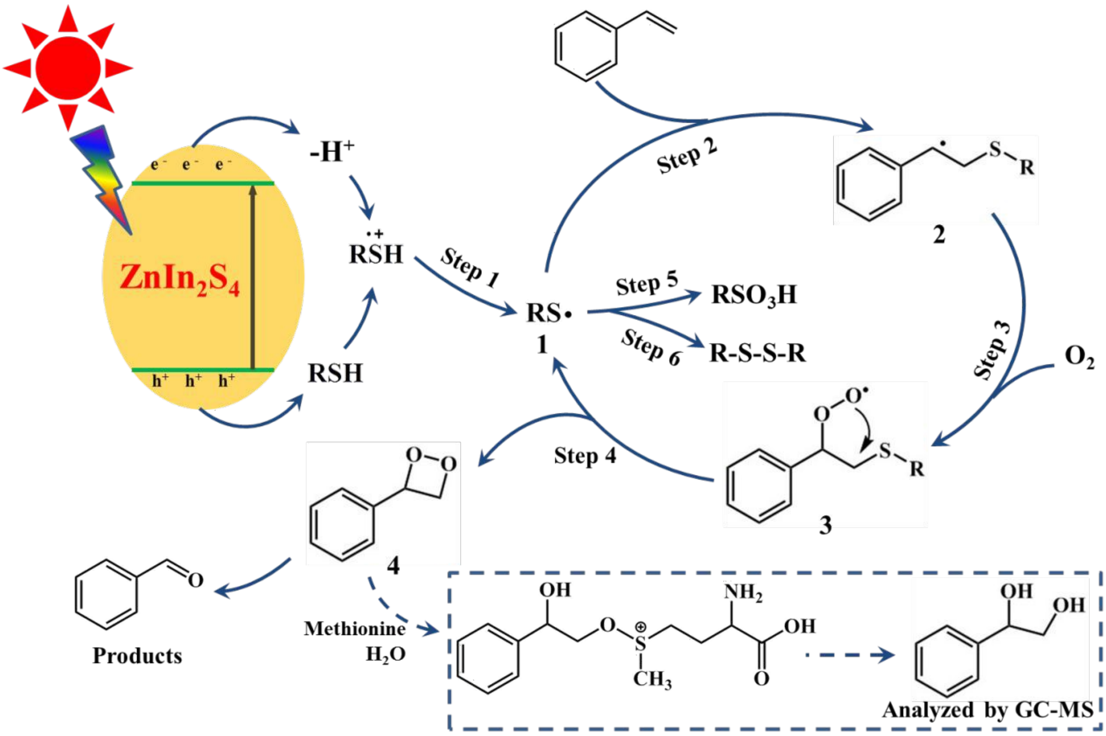
Scheme 1



Graphical Abstract

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