PAPER

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Visible-light-induced carbonylative atom transfer radical addition of alkenes: straightforward preparation of branched unsaturated thioesters

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Carbonylation is a straightforward methodology for the preparation of carbonyl-containing compounds, which are one of the core classes of compounds in pharmaceutical chemistry and industrial production. Among the developed carbonylation procedures, methods for branched unsaturated compounds are much less studied compared with their linear derivatives. However, their unique chemical structure and properties make them irreplaceable in numerous fields. Herein, we report a new visible-light-induced photocatalytic carbonylative atom transfer radical addition reaction of alkenes. The reaction proceeds effectively with 100% atom efficiency and produced various thioesters in good yields. Then, the product also led to efficient synthesis of branched unsaturated thioesters by simple base-mediated desulfonylation with recyclable arylsulfinic acid eliminated. Remarkably, besides their own importance, thioesters can also be used as acyl donors to produce important compounds such as ketones, aldehydes, esters, amides, and acyl silicon reagents.

1 Introduction

Carbonyl-containing compounds are among the most important chemicals in pharmaceutical chemistry and advanced materials. Their unique chemical structure gives them a wide range of transformation possibilities, making them essential in basic organic synthesis, materials science and pharmaceutical chemistry.[1–8] Carbonylation is an ideal methodology for the preparation of carbonyl-containing compounds and is advantageous due to its easily scalable production with carbon monoxide as a readily available C_1 source. Catalyzed by a suitable catalyst (Pd, Rh, Co, Ni or Cu), carbon monoxide can react with various substrates, such as alkenes, alcohols, amines and halogenated hydrocarbons, to give the corresponding carbonylated products. Numerous carbonyl-containing organic compounds can be readily generated with high atom economy, including aldehydes, carboxylic acids, amides, ketones, esters, thioesters and so on (Fig. 1a).[9–15] Among them, branched unsaturated carboxylic acid derivatives are

a key class of carbonyl-containing compounds extensively applied in industry. Their unique chemical structures and properties make them invaluable in many fields, including coatings and adhesives, healthcare, textiles and leather, electronics and optics, and papermaking. They are also important synthetic intermediates in organic chemistry and have been used to construct complex organic molecular skeletons through reactions such as addition, cyclisation and coupling.[16–29] They are also used to synthesize drug molecules, natural products and functional materials, such as methacrylic acid compounds including MMA, EMA, BMA, HEMA, MACl and MAPA. Among them, methyl methacrylate (MMA) is a key synthetic raw material for polymethyl methacrylate (PMMA), with an annual global market size as high as 6.4 million tonnes (Fig. 1b),[30] and plays an irreplaceable role in many fields due to its active chemical properties and excellent processing performance. In industry, MMA is produced by metal-catalyzed carbonylation of ethylene and then condensation with formamide (known as the Lucite alpha process). In comparison, procedures for branched unsaturated compounds are much less studied compared with their linear derivatives.

The efficient synthesis of methacrylic acid compounds has long been an attractive area of research for chemists. Decades of development have resulted in a variety of synthetic

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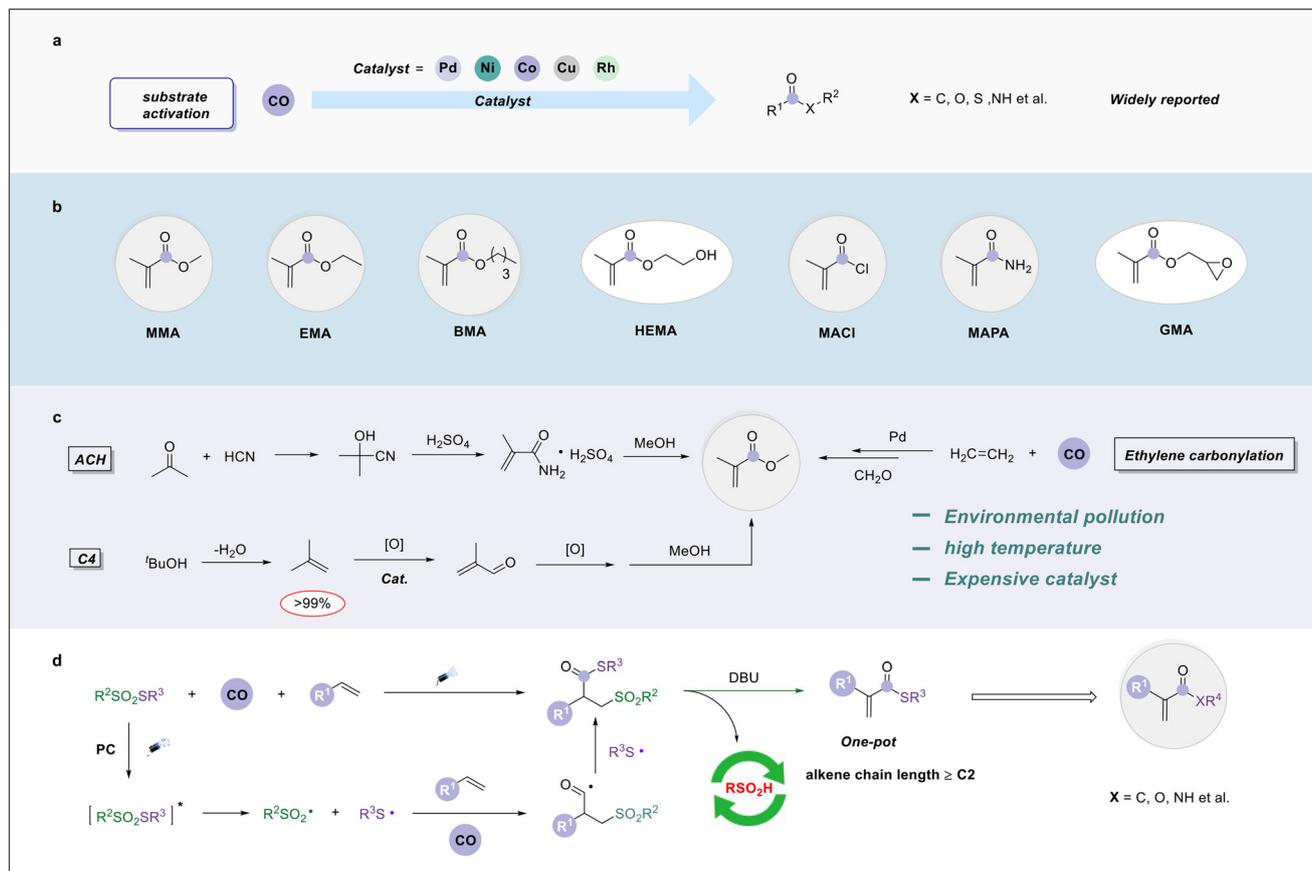
Fig. 1 Background and introduction to the carbonylation of α,β-unsaturated thioesters using CO. (a) Examples of CO applications in chemical synthesis; (b) important α,β-unsaturated carboxylic acid derivatives in industrial synthesis; (c) industrial application pathway for the preparation of MMA; (d) this work: synthesis of α,β-unsaturated thioesters from unactivated alkenes *via* visible light-induced photocatalysis.

pathways, each with significant differences in terms of the cost of raw materials, environmental friendliness and process complexity. The ACH method was the first industrialized MMA synthesis route and has been widely used due to the low cost and availability of its raw materials (acetone and hydrocyanic acid), accounting for 60% of global annual production. However, the high toxicity of the raw material hydrocyanic acid and the environmental pollution caused by its by-products as the main drawbacks make this process outdated technology. In the 1980s, the application of the isobutylene oxidation method gradually expanded due to the increasing availability of C₄ fractions in the refining industry and growing environmental protection requirements. It currently accounts for around 35% of global production capacity. Isobutylene or *tert*-butyl alcohol as its raw materials are relatively non-toxic and environmentally friendly, as well as highly atom-economical. However, this method suffers from complex production steps, high catalyst requirements and high reaction temperature. The synthesis of MMA by ethylene carbonylation is an important production process. It boasts advantages such as inexpensive and readily available raw materials, a short production process and low equipment investment costs, making it a promising technology. Nevertheless, expensive catalysts such as rhodium or

palladium are compulsory (Fig. 1c).[31–33] Therefore, exploring efficient and environmentally friendly synthesis methods remains in high demand.

Alkenes are one of the most important carbon-based resources in chemical industry, and their carbonylative difunctionalization reactions have been widely explored.[34–40] However, the direct preparation of branched unsaturated carboxylic acid derivatives is still relatively rare and challenging. Considering the rationality of the reaction design, we found that sulfonyl radicals can readily eliminate and reconstruct the double bond when a carbonyl group is present in the β-position.[41] Given the high oxidation potential of unactivated aliphatic alkenes, we envisaged visible-light-induced photocatalytic carbonylation of thiosulfonates *via* homolytic addition to alkene as a feasible route for preparing branched unsaturated thioesters. Furthermore, thioesters are often used as acyl donors to obtain important compounds such as ketones, aldehydes, esters, amides, and acylsilyl groups due to their excellent stability in air and poor orbital overlap compared to other ester analogues.[42–49] Moreover, the eliminated arylsulfinic acid can be recovered in an easy manner, which increases the overall atomic utilization (Fig. 1d).

2 Results and discussion

To implement the above synthetic method, we selected *S*-phenyl benzenesulfonothioate (**2a**) and hex-1-ene (**1a**) as the template substrates for systematic studies. After a series of reaction condition explorations, we found that the above design was feasible, and the target product was obtained successfully. After extensive research on the reaction parameters, the optimal conditions were obtained. In acetonitrile solution in the presence of [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (0.5 mol%), hex-1-ene (**1a**) (2.0 equiv.) was reacted with *S*-phenyl benzenesulfonothioate (**2a**) (1.0 equiv.) at room temperature for 48 hours to afford compound **3ab** in 65% yield. Compound **3ab** was then desulfonylated with DBU to give compound **4ad** in 55% yield (Fig. 2a). Other metal photocatalysts, such as ruthenium and iridium, could also produce the target compound, but with relatively low yields (Fig. 2b). We also screened the CO pressure required; the yield of product **3ab** was decreased to 31% when the pressure of CO was reduced from 60 bar CO to 40 bar. The yield of **3ab** decreased to 9–20% when the reaction was performed in other solvents. In the absence of a photocatalyst, the reaction yielded only 7% of **3ab**, and in the absence of light, the target compound was not obtained, even at evaluated reaction temperature. It is worth mentioning that a non-carbonylation product was the main side product detectable during the optimization process.

2.1 Evaluating the reaction scope

After determining the optimal conditions for the visible-light-induced carbonylation of alkenes, we tested the versatility of various substrates (Table 1). First, we examined the effects of various unactivated alkene substrates. For linear unactivated alkenes with varying lengths, from ethylene to oct-1-ene, we found that the target products (**3aa–3ae**) were all obtained in moderate to good yields under standard conditions. Notably, when using ethylene or propylene as the substrate, we achieved smooth conversion using a mixture of 10 bar of alkene gas and 50 bar of carbon monoxide, demonstrating the excellent applicability of this reaction with gaseous alkenes. Then, internal alkenes (**3af** and **3ag**) were checked under the standard conditions; the cyclic internal alkene reacted smoothly and gave the desired product in 45% yield, but no target compound was detected with the linear internal alkene. These phenomena might be due to the reason that the cyclic internal alkene is strained and activated while the linear internal alkene is not. We then examined substrates containing various substituents on the linear alkene chain. Cyclohexyl-substituted alkenes yielded only 42% (**3ah**), possibly due to its steric hindrance. Halogen-substituted alkenes also gave moderate to good yields of the desired products successfully (**3ai** and **3aj**). To further demonstrate the influence of substituents, we further investigated allylbenzene and its aryl variations, as well as but-3-en-1-ylbenzene (**3ak–3an**). The desired products can be obtained in moderate yields without any problem, even with *ortho*-bromo substituted and *para*-methoxy substituted substrates. However, no desired product was detected when styrene or butyl acrylate was tested.

Next, we examined the substrate versatility of thiosulfonates under optimal conditions (Table 2). We first investigated thiosulfonates containing electron-rich groups (including methyl, isopropylene, *tert*-butyl, and methoxy), which afforded the desired products in moderate to good yields (**3ba–3bg**). The naphthalene substituted substrate can also give the corresponding product in 42% yield (**3bh**). Notably, thiosulfonates substituted with an *ortho*-methyl group resulted in the highest yield compared with those
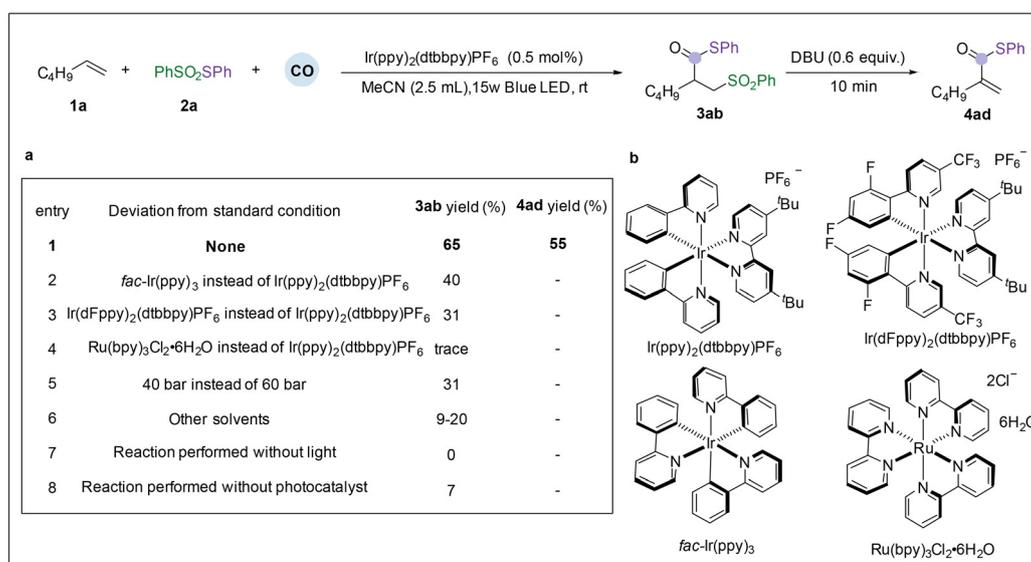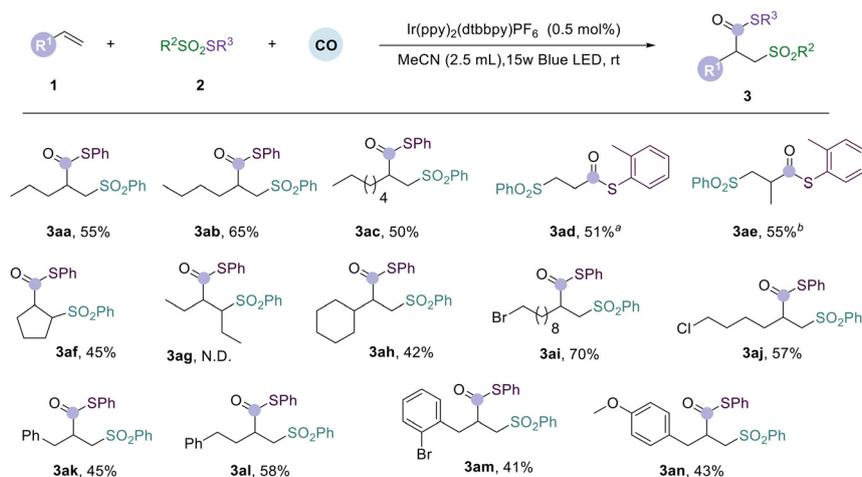

entry	Deviation from standard condition	3ab yield (%)	4ad yield (%)
1	None	65	55
2	*fac*-Ir(ppy)₃ instead of Ir(ppy)₂(dtbbpy)PF₆	40	–
3	Ir(dFppy)₂(dtbbpy)PF₆ instead of Ir(ppy)₂(dtbbpy)PF₆	31	–
4	Ru(bpy)₃Cl₂·6H₂O instead of Ir(ppy)₂(dtbbpy)PF₆	trace	–
5	40 bar instead of 60 bar	31	–
6	Other solvents	9–20	–
7	Reaction performed without light	0	–
8	Reaction performed without photocatalyst	7	–

Fig. 2 One-pot preparation of branched unsaturated thioesters. (a) Substrates **1a** and **2a** undergo visible light–induced difunctionalized carbonylation *via* addition of unactivated alkenes under a CO atmosphere. Product **3ab** undergoes desulfonylation to afford the unsaturated product; (b) photocatalysts.
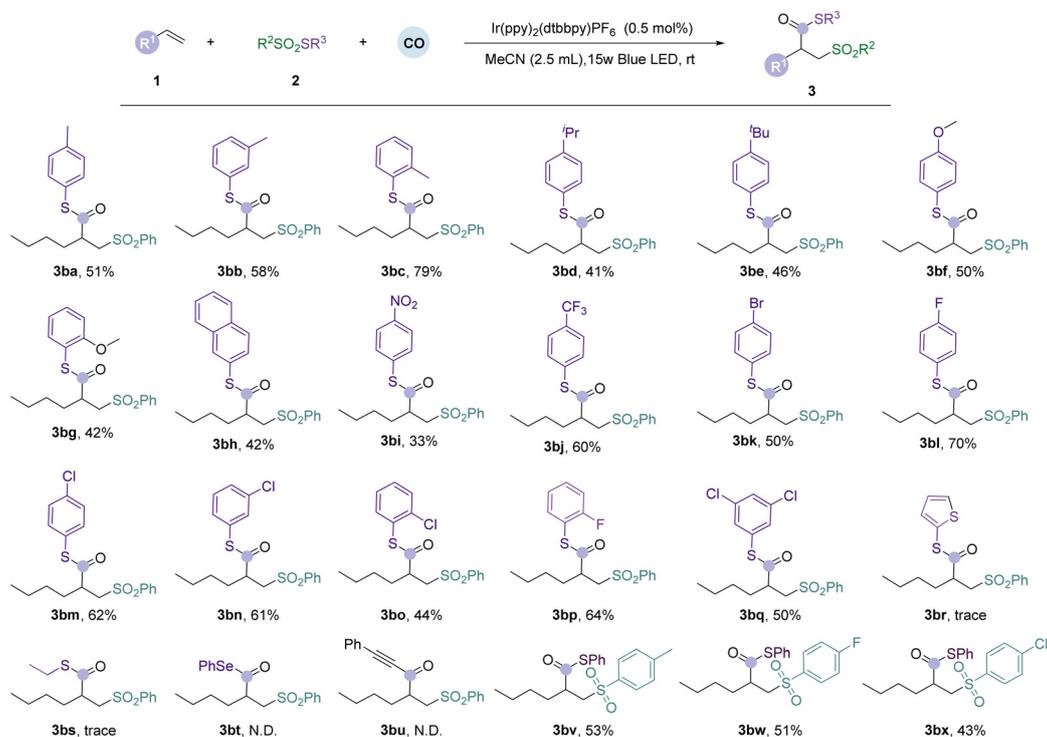
Table 1 Scope of unactivated alkenes

General conditions: **1** (0.2 mmol), **2** (0.1 mmol), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.5 mol%), in MeCN (2.5 mL) at rt for 48 h under CO (60 bar), irradiated by 15 W blue LEDs. All yields are isolated yields. ^{a} Ethylene (10 bar), CO (50 bar). ^{b} Propylene (10 bar), CO (50 bar).

Table 2 Scope of thiosulfonates

General conditions: **1** (0.2 mmol), **2** (0.1 mmol), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.5 mol%), in MeCN (2.5 mL) at rt for 48 h under CO (60 bar), irradiated by 15 W blue LEDs. All yields are isolated yields.

substituted with *meta*- and *para*-methyl groups (**3bc**), likely due to steric hindrance. However, when *ortho*-methoxy substituted thiosulfonate was tested under the same conditions, the reaction outcome did not meet the expectation (**3bg**). We then investigated the compatibility of thiosulfonates substituted with electron-withdrawing groups

(nitro, trifluoromethyl, chloride, bromide, and fluoride), which were successfully transformed to the desired products in moderate to good yields (**3bi–3bq**). We found that with fluoride- and chloride-substituted thiosulfonates, the yields of *ortho*- and *para*-substituted thiosulfonates were lower. When testing thiophene- and alkyl-substituted substrates

(**3br** and **3bs**), only a small amount of the target compound was detected. When using Se-phenyl benzenesulfonoselenoate and ((phenylethynyl)sulfonyl) benzene as the substrates, no expected products (**3bt–3bu**) were detected. We then tested sulfonyl-substituted substrates, including *para*-substituted methyl, fluorine, and chlorine (**3bv–3bx**), which afforded the corresponding products in moderate yields in all cases.
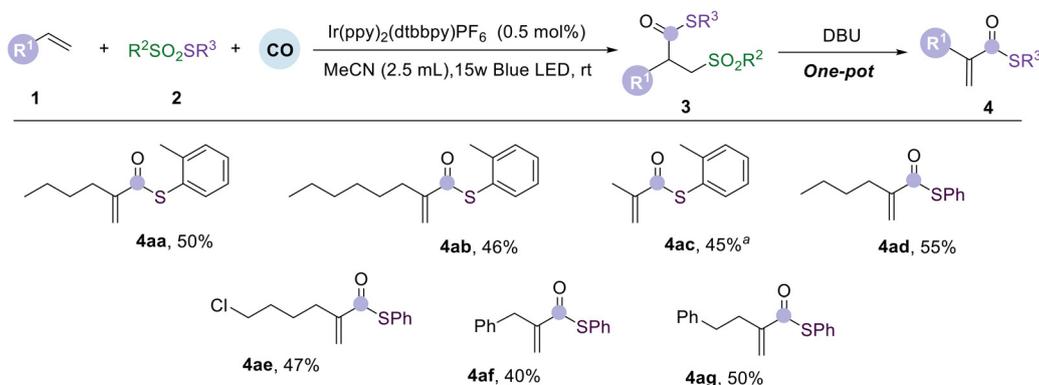
Based on the above discussed substrate studies, we attempted a one-pot, two-step approach to obtain branched unsaturated thioesters (Table 3). We examined alkene substrates of varying chain lengths and found that they could be obtained in moderate yields (**4aa–4ad**). Subsequently, we explored chlorine- and phenyl-substituted alkenes, and also afforded the desired unsaturated thioesters in moderate yields (**4ae–4ag**). This demonstrates that this reaction can successfully provide branched unsaturated thioesters conveniently in a one-pot, two-step approach.

Under optimal conditions, we also attempted to scale up the substrate reaction, and we still obtained the target product in 51% yield with a 1 mmol scale (Fig. 3a). Furthermore, we attempted to polymerize S-phenyl 2-methylprop-2-enethioate; a colorless solid was obtained successfully with promising molecule weight (Fig. 3b). The obtained unsaturated thioester can also be converted to the corresponding unsaturated ester easily (Fig. 3c). Furthermore, 44% yield of the desired product can be produced even in the absence of a photosensitizer by replacing light with 365 nm LEDs (Fig. 3d).

2.2 Mechanism studies

To further explore the mechanistic pathway of this reaction, we conducted a series of control experiments, as shown in Fig. 4. We attempted to verify the involvement of radical intermediates by adding radical inhibitors, such

Table 3 One-pot preparation of α,β-unsaturated esters

General conditions: step 1: **1** (0.2 mmol), **2** (0.1 mmol), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.5 mol%), in MeCN (2.5 mL) at rt for 48 h under CO (60 bar), irradiated by 15 W blue LEDs. Step 2: DBU (0.6 equiv.), 10 min, rt. All yields are isolated yields. [a] Propylene (10 bar), CO (50 bar).
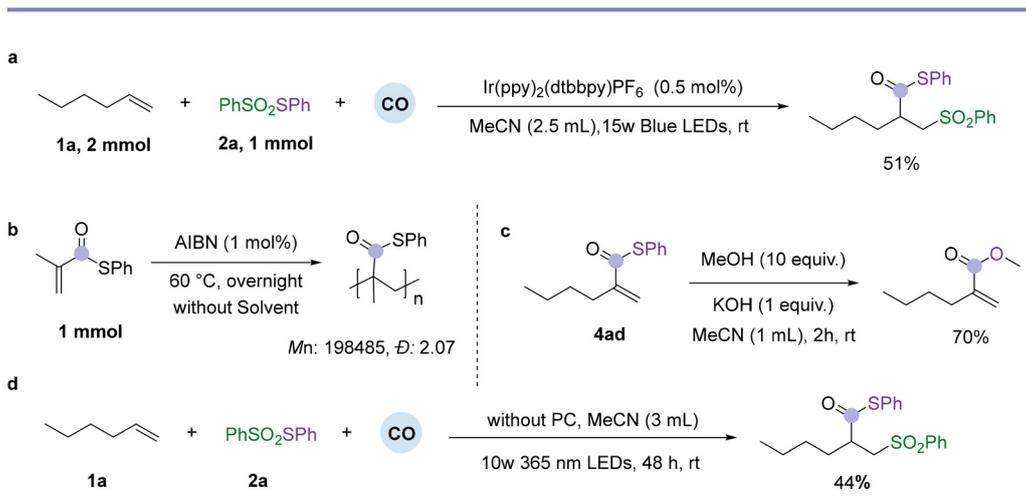

Fig. 3 Product transformations and scale-up reactions. (a) Reaction scaled up to 1 mmol; (b) polymerization of unsaturated thioesters; (c) conversion of unsaturated esters; (d) reaction without photocatalysis.

as TEMPO and BHT. First, no target product could be detected after 3 equivalents of TEMPO were added under standard conditions (Fig. 4a). Additionally, only a small amount of the target product was produced when 3 equivalents of BHT were added (Fig. 4b). These results suggest that the reaction may undergo a radical mechanism. Furthermore, we attempted a 1:1 reaction of S-phenyl benzenesulfonothioate and S-(4-chlorophenyl) 4-chlorobenzenesulfonothioate under standard conditions. We detected the formation of both S-(4-chlorophenyl) benzenesulfonothioate and S-phenyl 4-chlorobenzenesulfonothioate, further confirming the possibility of radical involvement (Fig. 4c). However, in the absence of light, no reaction occurred, leading us to speculate that the thiosulfonate reacts *via* homolytic cleavage. When we added 1,2-bis(4-chlorophenyl)disulfane to the template reaction, two mixed products were detected (Fig. 4d). The reaction with only 1,2-bis(4-chlorophenyl)disulfane, in the absence of thiosulfonate, will lead to β-thiopropionate thioester formation.[50] To verify whether sulfinic acid was produced after desulfonylation, we tried adding NaOH and water for extraction after the desulfonylation step. We detected sodium benzenesulfinate salt, and the resulting mixture could be used directly as a synthetic raw material for substate preparation (Fig. 4e).

2.3 Possible mechanism

Based on the above experiments and results, we proposed a possible reaction mechanism (Fig. 5). First, compound **B** is excited by the excited photosensitizer and homolytically splits into a sulfonyl radical and a phenylthiol radical. The sulfonyl radical is then added to the unactivated alkene **A** to form intermediate **C**. Under carbon monoxide pressure, intermediate **C** captures carbon monoxide to form acyl radical intermediate **D**. In the presence of a phenylthiol radical or disulfide, product **E** is obtained finally. Product **E** can then be desulfonylated by DBU to produce product **F**.

3 Conclusions

In summary, we have developed a novel visible-light-induced carbonylation method for the synthesis of branched unsaturated thioesters. This reaction involves homolytic addition of thiosulfonates to unactivated alkenes, followed by carbonylative difunctionalization under the action of carbon
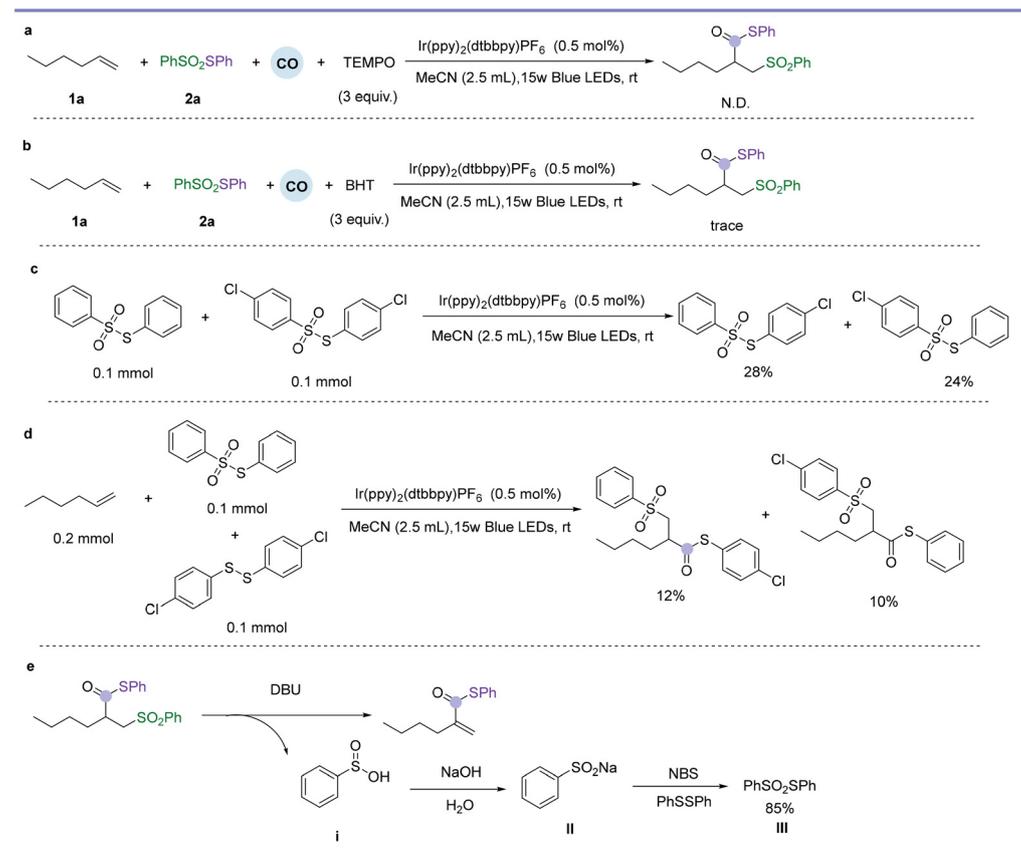

Fig. 4 Mechanistic studies. (a) TEMPO radical capture experiment; (b) BHT radical capture experiment; (c) disulfide exchange experiment; (d) competitive reaction between thiosulfonate and disulfide; (e) benzenesulfinic acid verification experiment after desulfonylation.
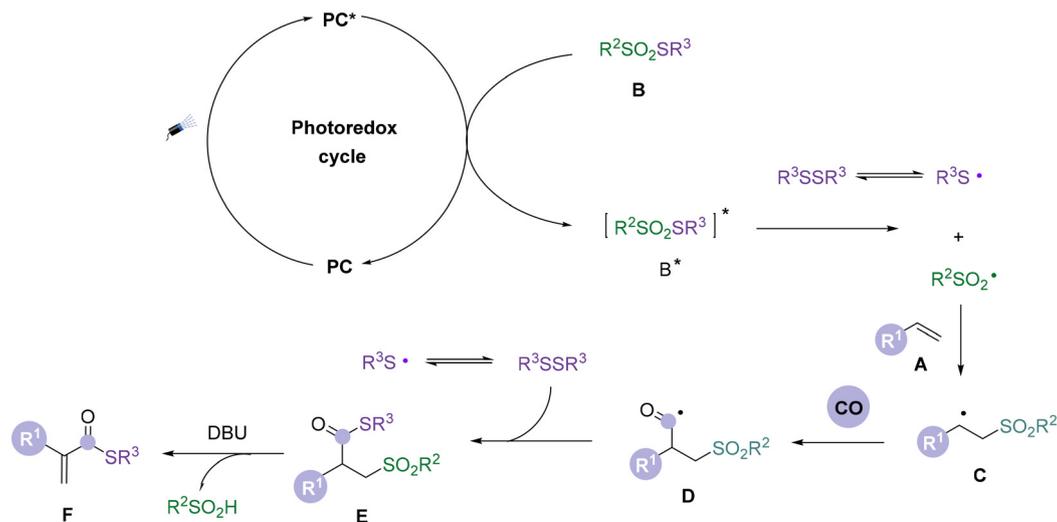
Fig. 5 Possible mechanism.

monoxide to afford thioesters. This reaction, while milder than previous methods for synthesizing α,β-unsaturated carboxylic acid derivatives, afforded a variety of valuable branched unsaturated thioesters in moderate to good yields. The reaction also exhibited good tolerance for a wide range of functional groups. Furthermore, the difunctionalized carbonylation of thiosulfonates *via* homolytic cleavage demonstrated high atom utilization up to 100%.

4 Methods

1 (0.2 mmol), **2** (0.1 mmol), Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.5 mol%), and an oven-dried stir bar were placed in a 4 mL screw-capped vial. The vial was sealed with a Teflon septum and cap and vented to the atmosphere *via* a needle. MeCN (2.5 mL) was then added *via* a syringe under a nitrogen atmosphere. The sealed autoclave was flushed twice with nitrogen (10 bar) and filled with 60 bar of CO. The reaction mixture was stirred at room temperature under 15 W blue LEDs (450–460 nm) for 48 hours. After the reaction was complete, the pressure was carefully released. DBU (0.6 equiv.) was added to the reaction solution and stirred at room temperature under air for 10 minutes. The mixture was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (PE/EA = 50/1) to obtain the corresponding product. It is important to note that unsaturated thioesters readily decompose in DBU, so the product should be handled promptly after the reaction.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI).

Supplementary information is available. See DOI: https://doi.org/10.1039/d5im00399g.

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