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## Photocatalysis

# A Naphthalimide-Based ND-O-EAc Photocatalyst for Sulfonation of Alkenes to Access β-Ketosulfones Under Visible Light

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**Abstract:** The development of facile, efficient, cost-effective, and visible light-driven photocatalysts for organic synthetic chemistry has received increasing attention. This protocol has initially synthesized a naphthalimide-based ND-O-EAc visible light photocatalyst for the sulfonation of alkenes to produce β-ketosulfones. Compared with the current photosynthetic strategies, the newly developed catalytic system has some merits, namely high efficiency, gram-scale preparation of low-cost photocatalyst, no metal contamination, wide substrate scope, and green terminal oxidant of air. Moreover, the prepared photocatalyst of ND-O-EAc is feasible for the sulfonation reactions of androstenones. Importantly, such a photocatalysis strategy can easily realize the scale-up synthesis for β-ketosulfone drugs under the mild conditions up to 90 % yield.

## Introduction

The visible light-driven photocatalysis as a green synthetic route has been given a great deal of attention from synthetic chemists achieving a series of valuable organic transformations.[1] In particular, the photocatalytic strategies using transition metal complex or organic dyes as photocatalysts have achieved a series of milestones in the past decade.[2] However, most of the current photocatalysts can encounter with some intrinsic challenges such as high cost, metal contamination, cumbersome synthesis route and low catalyst yield. To overcome these limitations, the development of visible light-induced, metal-free, highly efficient, cheap and readily available photocatalysts has received enormous attention from chemists.[2a,3] Nevertheless, the readily available dyes as efficient photocatalysts, especially those with naphthalimide-based frameworks under visible light have rarely been reported for organic transformations in constructing highly bioactive drug blocks.[4]

As a powerful and fascinating strategy, the bifunctionalization of olefins has attracted significant interest from chemists due to it can provide an efficient way to form new carbon–carbon and carbon–heteroatom bonds in one operation.[5] Through this methodology, many useful functional groups could be introduced into alkenes to access a series of important organic frameworks.[6] In the last decade, the synthesis of β-ketosulfones has been successfully achieved through the difunctionalization of olefins mediated by transition metal or dye

catalyzed with stoichiometric chemical oxidants (Figure 1a).[6f,7] Particularly, Ydadv et al. developed a direct approach to β-ketosulfones via AgNO$_3$/K$_2$S$_2$O$_8$ catalyzed oxysulfonylation of alkenes with arenesulfinate slats or thiophens.[7d,7h]
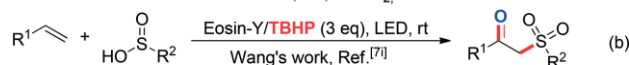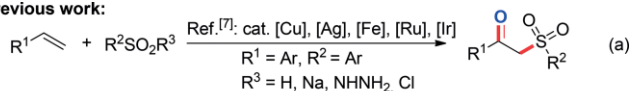


Figure 1. Advantage of ND-O-EAc induced bifunctionalization of alkenes.

Moreover, the sulfonation of alkenes to β-ketosulfones has also been successfully implemented by our group, based on eosin-Y as a photocatalyst, and stoichiometric *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant under visible light irradiation conditions (Figure 1b).[7i] In spite of numerous achievements so made, most of these methods may suffer from some limitations, namely high cost, metal contamination, cumbersome photocatalyst synthesis route, stoichiometric chemical oxidants and poor substrate scope. Therefore, it is highly desirable to develop more efficient, metal-free, environmentally-benign, cheap and readily available catalysts for the photocatalytic bifunctionalization of alkenes to access the biologically active β-ketosulfones. In the continuation of our efforts in devel-

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oping new type of visible-light catalysts for constructing sulfone-containing compound,[8] herein, we wish to report an efficient and readily available visible light-driven photocatalyst of ND-O-EAc for the photocatalytic bifunctionalization of alkenes to access the β-ketosulfones simply by using air as the terminal oxidant (Figure 1c).

Overall, compared with the previous work, the ND-O-EAc-induced sulfonation of alkenes to access the β-ketosulfones has the following merits: **(1)** the synthesis method of photocatalyst can be simply synthesized on a large scale; **(2)** any transition metals or chemical oxidants are not entailed; **(3)** excellent tolerance of functional groups and outstanding gram-scale yields can be expected.

## Results and Discussion

### Gram-Scale Synthesis of ND-O-EAc Photocatalysts

Visible light-driven photocatalysts were synthesized using a procedure from our previously published.[4d,4g] The main reason for choosing N-substitution is that the reaction of acid anhydride and amine can facilitate the modification of photocatalyst structure, and the purpose of selecting poly-hydroxylate chain is to improve the solubility of the photocatalyst. Thence, the synthesis route of 2-{2-[1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl] ethoxy}ethyl acetate (ND-O-EAc), 2-{2-[(2-hydroxyethyl)(methyl) amino]ethyl}-6-(piperidin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H) -dione (ND-N-EAc), and 2-{2-[1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl]-ethoxy}ethyl acrylate (ND-O-EA) were described in Figure 2. A series of naphthalimide-based photocatalysts ND-N-EAc, ND-O-EAc, and ND-O-EA can be synthesized on the gram scale. In particular, ND-O-EAc was able to obtain a yield of 75 % on a scale of 10 mmol.
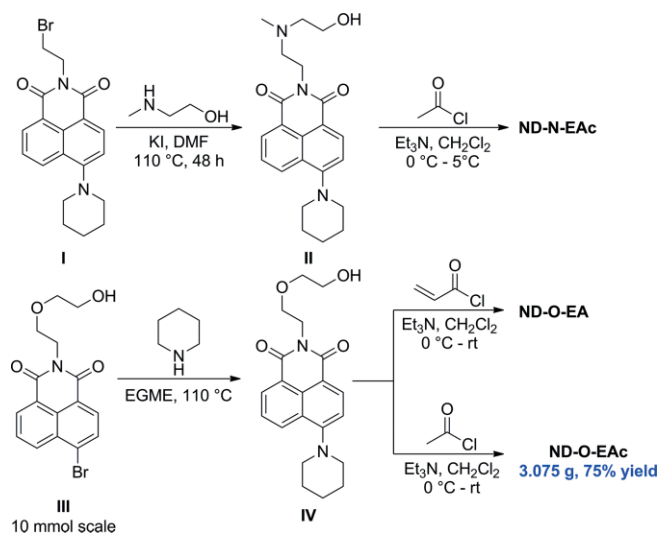


Figure 2. Gram-scale synthesis of photocatalysts.

### Optical and Redox Potential Characterization

The optical and redox potential characterization of photocatalysts of ND-O-EAc was carried out separately by UV spectroscopy and cyclic voltammetry (CV). First and foremost, by comparing the UV/Vis absorption spectra of ND-O-EAc and III in acetonitrile (Figure 3a), it can be seen that the maximum absorption and emission wavelength of ND-O-EAc were located at 406 nm and 535 nm when the alkylamino was introduced at the 4-position of naphthalimide. This result confirms that ND-O-EAc has an excellent absorption performance for blue LEDs in the visible light region. Subsequently, in order to investigate the redox capacity of ND-O-EAc, the CV experiment was conducted in an acetonitrile solution with $n\text{Bu}_4\text{NBF}_4$ as the electrolyte. Compared with our previous single-atom-site iron catalyst CNH (1.15 V vs. Ag/AgCl), an oxidation peak of ND-O-EAc in acetonitrile was observed at 1.19 V (vs. Ag/AgCl) in the positively charged partial region (Figure 3b).[8] Therefore, it is thought that the excited state of ND-O-EAc might be more easily oxidize p-methylbenzenesulfinic acid than CNH under the visible light irradiation conditions.
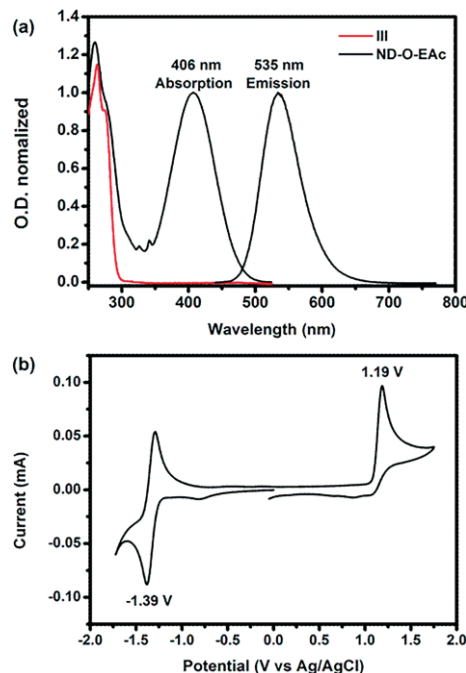


Figure 3. (a) UV/Vis absorption spectra of ND-O-EAc and **III** ($c = 8 \times 10^{-5}$ mol/L), $\lambda_{int}$ = 480.5 nm. (b) Cyclic voltammetry results of ND-O-EAc, $n\text{Bu}_4\text{NBF}_4$ (0.1 M), scan rate of 100 mv/s.

### Investigation of Photocatalytic Performance

To confirm our conjecture, the styrene (**1a**) and p-methylbenzenesulfinic acid (**2b**) were chosen as the model substrates to perform reaction utilizing the ND-O-EAc instead of CNH as the photocatalyst. As excepted, the desired product **3ab** could be obtained in a 95 % yield when using ND-O-EAc (2.5 mol-%) instead of single-atom iron site biomimetic photocatalytic CNH (carbon nitride with hemin, 4.5 mol-%, yield: 94 %) in the absence of hydrochloric acid and irradiating 36 h with a blue LEDs (Table 1, entry 1).[8] The control experiments show that no product was observed in the absence of photocatalyst and light (Table 1, entries 2–3). Subsequently, the efficiency of the reac-

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tion was not improved either by increasing or decreasing the concentration of the photocatalyst (Table 1, entry 4). Thereafter, desired products **3ab** had only moderate yields when the ND-O-EA, ND-N-EAc and **III** were used as photocatalysts (Table 1, entries 5–6). The photocatalyst ND-O-EA contains an acrylic ester structure, which will participate in the photopolymerization of olefins and cause catalyst loss. However, the photocatalyst ND-O-EAc can effectively avoid the photopolymerization process. Moreover, the low yield of ND-N-EAc may be caused by the oxidation of the amino group by the photocatalyst in it excited state. Alternatively, only trace amounts of the products could be obtained when replacing the ambient conditions with a nitrogen atmosphere, which indicates that the carbonyl oxygen in the product may originate from air (Table 1, entry 7). Moreover, the optimization of the reaction solvent revealed that CH_3CN was the best choice (Table 1, entries 8 –12). Therein, only trace amounts of desired products were generated when the reaction was performed in DMF or MeOH. The reason is presumed that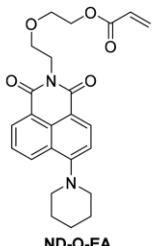 the photocatalyst has stronger oxidizing ability in DMF than CH_3CN, which leads to peroxidative decomposition products.
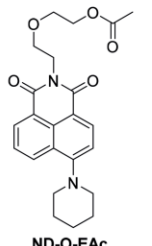
## Substrate Scope

With the optimized conditions above, the scope and limitations of the reaction of various alkene (**1**) substrates were explored using p-methylbenzenesulfinic acid (**2b**), with the results shown in Table 2. As expected, a variety of alkenes with electron-donating or electron-withdrawing substituents on the aryl groups were found to be suitable for this protocol, and the corresponding products were obtained in good yields (**3ab** - **3ib**). Halide substituents such as F, Cl, Br and CF_3 were well tolerated under the standard conditions, furnishing the β-ketosulfones in high yields. Moreover, the sterically congested meta- and ortho-substituted substrate were also efficiently reacted with p-methylbenzenesulfinic acid (**2b**) to give the products **3hb** and **3ib** in 75 % and 83 % yields, respectively. However, the desired product **3jb** was only obtained in 18 % yield when the terminal olefins replaced with internal olefins. Besides, the desired products were obtained in moderate yield when 1H-indene and 1,2-dihydronaphthalene were performed under standard conditions, while a hydroxylated product was present in **3lb**. Subsequently, the hydroxylated products of **3mb** and **3nd** were also obtained when styrene was replaced by cyclohexene and androstenones, respectively. These results indicate that the hydroxylated products should be the intermediates of the sulfonation reactions. Notably, the 2-vinylthiophene was performed under the prevailing conditions, and the desired products **3ob** could also be obtained in a good yield. Unfortunately, the protonated product **3pb** was obtained with high selectivity without the formation of β-ketosulfone when N-heterocyclo-olefin was subjected to the standard conditions. Subsequently,
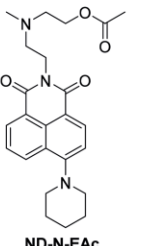
Table 1. Optimization of the reaction conditions.[a]



| Entry | Deviation from standard conditions | Yield (%)[b] |
|---|---|---|
| 1 | none | 95 (94[c]) |
| 2 | without ND-O-EAc | N. D. |
| 3 | without light | N. D. |
| 4 | 1.25 % or 5 % instead of 2.5% | 31 - 78 |
| 5 | ND-O-EA, ND-N-EAc instead of ND-O-EAc | 23 - 58 |
| 6 | **III** instead of ND-O-EAc | 45% |
| 7 | N_2 instead of air | trace |
| 8 | DMF or MeOH instead of CH_3CN | trace |
| 9 | Toluene instead CH_3CN | 57 |
| 10 | xylenes instead CH_3CN | 67 |
| 11 | DCE instead CH_3CN | 63 |
| 12 | 1,4-dioxane instead CH_3CN | 19 |
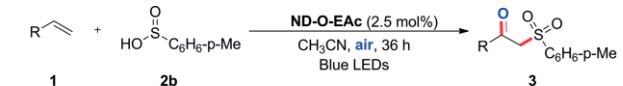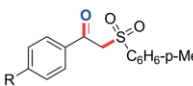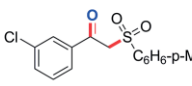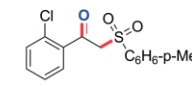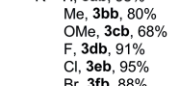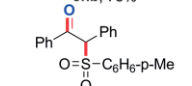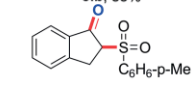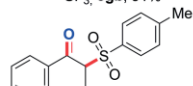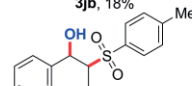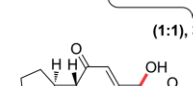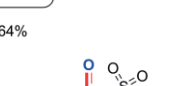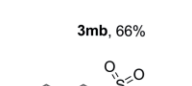


[a] Standard conditions: **1a** (0.5 mmol), **2b** (1.0 mmol), CH_3CN (2.0 mL), air, blue LEDs, r. t., and 36 h, "N.D." = not detected. [b] Isolated yield. [c] Our previous standard conditions.[8]

Table 2. Scope of the alkenes.[a,b]



[a] Reaction conditions: **1** (0.5 mmol), **2b** (1.0 mmol), ND-O-EAc (2.5 mol-%), CH_3CN (2.0 mL), air, blue LEDs, r. t., and 36 h. [b] Isolated yields.

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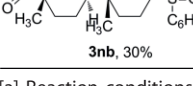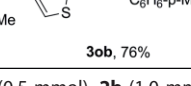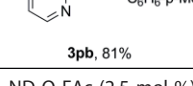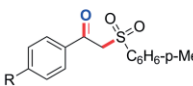European Chemical
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the scope of sulfinic acids was investigated, with the results shown in Table 3. Various substituted benzenesulfinic acids bearing either electron-rich or electron-deficient groups were all suitable for this protocol to give the corresponding products in good yields, thereby facilitating possible further modifications (**3aa** - **3ag**). Moreover, other kinds of sulfinic acids such as naphthalene-2-sulfinic acid and alkylsulfinates could also generate the desired products in good yields when the reaction solvent of standard conditions was replaced by DMF (**3ah** - **3aj**). It is speculated that the photocatalyst may have a lower reduction potential in DMF.

Table 3. Scope of sulfinic acids.[a,b]
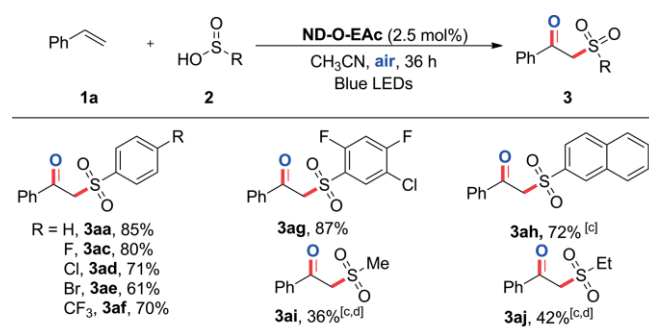


[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), ND-O-EAc (2.5 mol-%), $CH_3CN$ (2.0 mL), air, blue LEDs, r. t., and 36 h. [b] Isolated yields. [c] DMF instead of $CH_3CN$. [d] Sodium sulfinate.

Afterwards, the gram-scale reaction between styrene (**1a**) and 4-methylbenzenesulfinic acid (**2b**) afforded the desired product **3ab** in 90 % yield (Scheme 1), further highlighting the great potential application of this transformation.



Scheme 1. Gram-scale synthesis of **3ab**.

## Mechanistic Studies

To further understand the role of ND-O-EAc in this oxidative coupling mechanism of alkenes with sulfinic acids to form β-ketosulfones, a series of control experiments were performed based on the standard reaction conditions (Scheme 2). Firstly, the active species trapping experiments were conducted to clarify the contribution of different active species in the reactions. Accordingly, benzoquinone [BQ was selected to identify the active species superoxide radical ($O_2^{\cdot-}$)].[8,9] The yield of desired products was significantly decreased after adding the BQ, indicating that ND-O-EAc can generate superoxide radicals species ($O_2^{\cdot-}$) by visible light irradiation under the standard conditions (Scheme 2a). Subsequently, radical trapping experiments were carried out to confirm whether this reaction went through a radical reaction pathway. It was discovered that the sulfonation reaction was inhibited when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-tertbutyl –4-hydroxytoluene (BHT)

was added into the present reaction system, suggesting the reaction has presumably adopted a radical pathway (Scheme 2b). Moreover, the sulfone radical could be captured by 1,1-diphenylethylene (**1q**) under standard conditions (Scheme 2c, Figure S20). Additionally, desired products of 2-phenyl-1-tosylpropan-2-ol **3rb** in 25 % yield was observed, when the reaction of **1r** with **2b** proceeded under the standard conditions (Scheme 2d), demonstrating that the hydroxylated products should be the intermediates of the sulfonation reactions.[7i,8]
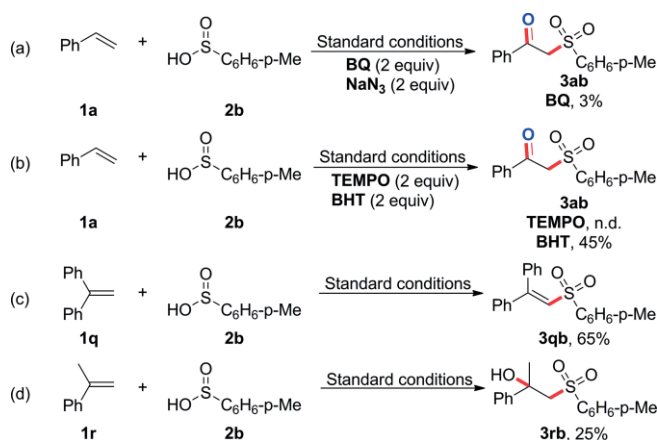


Scheme 2. Mechanism studies. (a) Active species trapping experiments. (b), (c) Radical trapping experiments. (d) The intermediate experiments.

Subsequently, to determine whether a reductive or oxidative quenching cycle is operative in a particular reaction, fluorescence quenching (or Stern–Volmer) studies are employed between a photocatalyst and 4-methylbenzenesulfinic acid **2b** or styrene **1a**. The result shows that the emission intensity of the excited photocatalyst was dramatically decreased along with the increasing of the concentration of **2b** ($k_q = 1.2 \times 10^8$ $M^{-1}S^{-1}$), which showed the occurrence of a direct interaction between the excited state of [ND-O-EAc]* and the ground-state substrate **2b** (Figure 4a and Figure 4b). In contrast, such an effect was not observed when styrene **1a** ($k_q = 3.6 \times 10^6$ $M^{-1}S^{-1}$) was added dependently, even if the concentration of **1a** was increased by 10,000 times (Figure 4c and Figure 4d). The above results strongly indicated that the photocatalyst should participate in reductive quenching with 4-methylbenzenesulfinic acid **2b** under the standard reaction conditions.[10d]

Finally, the switch visible light experiment was performed to investigate the effect of photo-irradiation. The results demonstrate that continuous irradiation with visible light should be required in the present transformation (Figure 5).

Based on the above preliminary results and referring to the previous reports,[1f,2a,2b,7i,8,10] a plausible pathway is proposed in Scheme 3. Initially, the photocatalyst ND-O-EAc was excited by visible light irradiation leading to the excited state species [ND-O-EAc]* {$E_{1/2 \text{ red}}$ [ND-O-EAc*/ND-O-EAc$^{\cdot-}$] = +1.19 V vs. Ag/AgCl, $E_0 = 2.58$ eV ($\lambda_{int} = 480.5$ nm)}, which could be reductively quenched by **2a**, generating the radical cation species **A** and [ND-O-EAc]$^{\cdot-}$ {$E_{1/2 \text{ red}}$ [ND-O-EAc$^{\cdot-}$/ND-O-EAc] = –1.39 V vs. Ag/AgCl, $E_0 = 2.58$ eV ($\lambda_{int} = 480.5$ nm)}.[10e,10f] Then, the oxidation of [ND-O-EAc]$^{\cdot-}$ by dioxygen (air) affords the ground state

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Figure 5. Switch light experiments.

radical **B** resonating with the sulfonyl radical **C**. Next, the resulting sulfonyl radical interacts with **1a** to produce the benzyl radical **D**, and the carbocation intermediate **E** is generated by the excited state species [ND-O-EAc]* oxidation of **D**. Finally, the nucleophilic attack of the $H_2O$ on the carbocation intermediate can produce the intermediate **E**, which would be transformed into the desired product **3aa** under the oxidative conditions (Path A). In addition, the benzyl radical **D** may be captured by dioxygen to generate peroxy radical **H**. Thereafter, the peroxy radical **H** interacted with ·OOH to form monoalkyl tetroxide intermediate and decomposed into the desired product **3aa** (Path B).[11] Further investigation of more detailed mechanisms is underway in our laboratory.
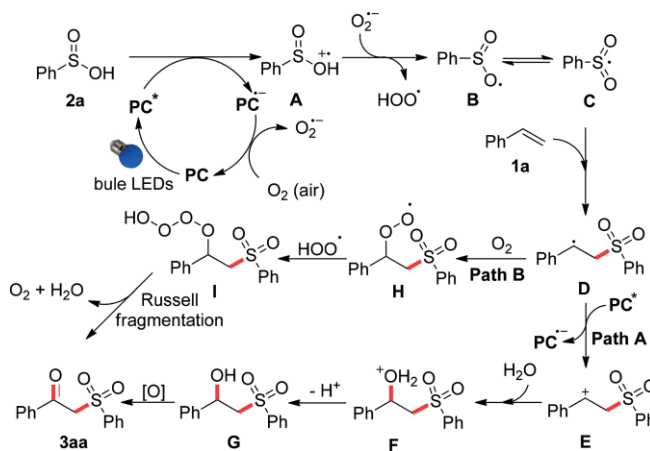


Scheme 3. Postulated reaction pathway.

## Conclusion

In summary, an efficient and readily available photocatalyst of ND-O-EAc has been developed for the construction of β-keto-sulfones. Taking into account the combination of desirable features, such as cheap and readily available photocatalysts, operation simplicity, product diversity, and metal-free catalysis conditions, this reaction system is expected to provide an alternative and attractive approach to a series of biologically important β-ketosulfones from sulfinic acids with alkenes. Importantly, the present protocol can be scaled up in good reaction efficiency,
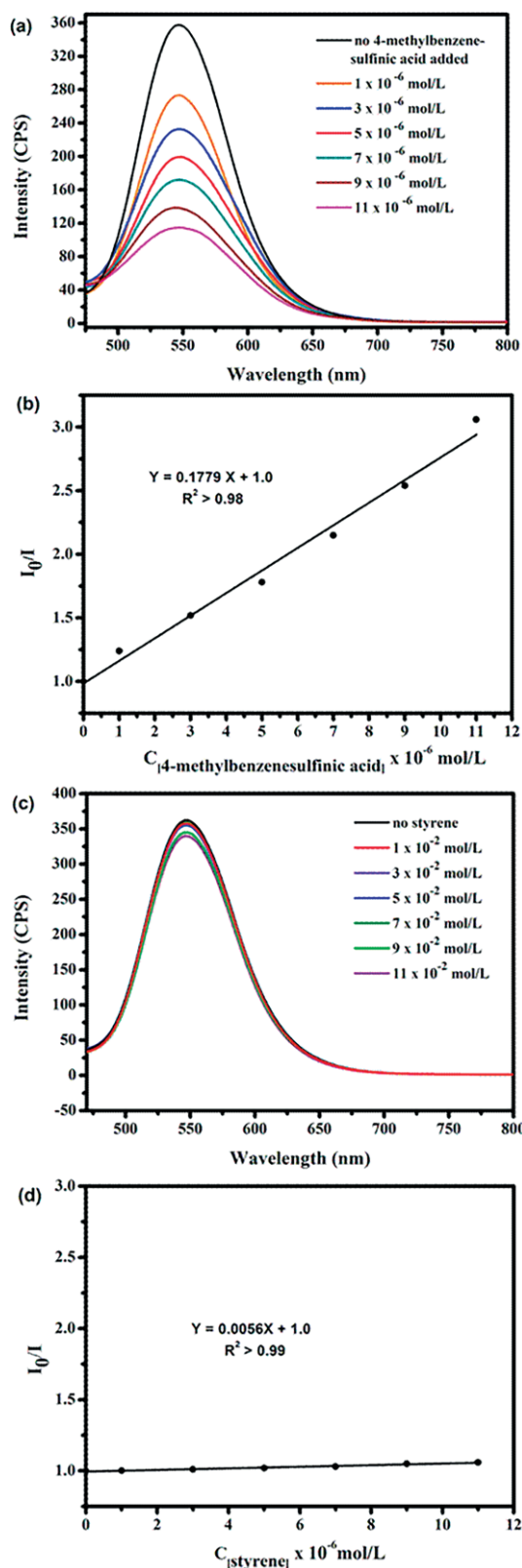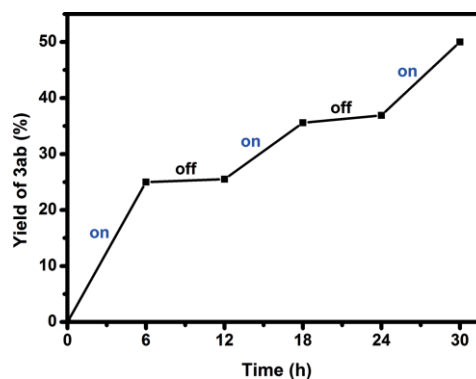
Figure 4. Quenching of ND-O-EAc ($\tau = 1.55$ ns) fluorescence emission in the presence of 4-methylbenzenesulfinic acid (a) or styrene (c). (b, d) Stern–Volmer plots. The excitation wavelength was fixed at 425 nm.

ND-O-EAc and superoxide radical species $O_2{}^{\cdot-}$. The radical cation **A** is deprotonated by $O_2{}^{\cdot-}$ leading to the oxygen-centered

which is beneficial for the widely practical applications. Further mechanism investigation and more realistic applications of this photocatalysis-based synthesis method are currently underway in our laboratory.

## Experimental Section

A Schlenk tube equipped with a stir bar was loaded with 5.2 mg (2.5 mol-%) of ND-O-EAc, alkenes **1** (0.5 mmol), and sulfonic acid/sodium **2** (1.0 mmol) in 2.0 mL of $CH_3CN$ under air atmosphere. The solution was then stirred at room temperature under the irradiation of blue LED lamps for 36 h, the set-up of experiments as shown in Figure S1. After the completion of reaction, the reaction mixture was washed with saturated potassium carbonate solution and extracted with $CH_2Cl_2$ (10 mL × 3). The organic layers were combined, dried with $Na_2SO_4$, and concentrated. Then, the pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl ether = 5:1–10:1) to afford corresponding products **3**.

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