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可见光辅助无光敏剂串联磺酰化-环化合成吲哚酮

巫晓婷[a] 赵 峰*[,b] 姬小趁[a] 黄华文*[,a,c]
([a]湘潭大学化学学院 湖南湘潭 411105)
([b]湖南医药学院药学院 湖南怀化 418000)
([c]河南师范大学化学化工学院 河南新乡 453007)

摘要 吲哚酮类的衍生物在许多领域具有重要应用, 这种特殊的杂环骨架以其独特的功能性在天然产物和生物活性分子中的应用越来越广泛. 因此探索新型的吲哚酮衍生物的合成方法非常重要. 报道了一种在可见光辅助下无光敏剂的磺酰化吲哚酮的高效合成方法. 该方法从简单易得的 *N*-芳基丙烯酰胺和芳基或烷基亚磺酸钠出发, 使用廉价的 $K_2S_2O_8$ 作为氧化剂, 具有中等至良好的产率及出色的官能团耐受性.

关键词 可见光诱导; *N*-芳基丙烯酰胺; 吲哚酮; 环化

Visible Light-Assisted Photocatalyst-Free Tandem Sulfonylation/Cyclization for the Synthesis of Oxindoles

Xiaoting Wu[a] Feng Zhao*[,b] Xiaochen Ji[a] Huawen Huang*[,a,c]
([a] *College of Chemistry*, *Xiangtan University*, *Xiangtan*, *Hunan 411105*)
([b] *School of Pharmaceutical Sciences*, *Hunan University of Medicine*, *Huaihua*, *Hunan 418000*)
([c] *School of Chemistry and Chemical Engineering*, *Henan Normal University*, *Xinxiang*, *Henan 453007*)

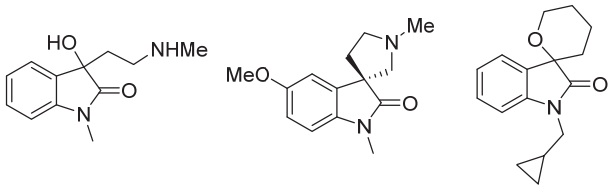
Abstract Oxindole derivatives are well developed in many fields, and this special heterocyclic scaffold is more and more widely used in natural products and bioactive molecules due to its unique functionality. Therefore, it is very important to explore new synthesis methods for this motif. A visible light-assisted photocatalyst-free protocol for the efficient synthesis of sulfonylated oxindoles under mild condition was reported. The present method starts from simple and readily available *N*-arylacrylamide and sodium sulfinates, uses cheap $K_2S_2O_8$ as oxidant, and features moderate to good yields and excellent functional group tolerance.

Keywords photocatalysis; *N*-arylacrylamide; oxindole; cyclization; photocatalyst-free

1 Introduction

Oxindoles are an important class of heterocyclic compounds with unique biological activities that are commonly found in many natural products and biologically active compounds.[1] (Figure 1) In particular, functionalized oxindoles have attracted extensive attention for their important synthetic applications.[2] Subsequently, chemists have explored various methods for the construction of oxindole derivatives.[3]

N-Arylacrylamides have received extensive attention as a common radical acceptor in addition/cyclization reactions[4]. This process provides versatile strategies for the construction of functional oxindoles.[5] Despite of great progress, there is still a need to develop mild and efficient methods for the synthesis of functionalized oxindoles. As



Donaxaridine Horsfiline CB2 agonist

Figure 1 Bioactive compounds containing oxindole skeletons

* Corresponding authors. E-mail: zhaofenghnmu@163.com; hwhuang@xtu.edu.cn
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an emerging green tool in organic synthesis, visible light-mediated photocatalysis has attracted broad interest among researchers due to the features regarding mild and environmental friendly conditions and simple operation.[6] It also provided powerful attractive methods for the synthesis of oxindole and its derivatives from *N*-arylacrylamides (Figure 2). Visible light-induced direct cyclization of *N*-arylacrylamides could generate oxindoles[7] or dihydroquinolinones (Figure 2 a).[8] Moreover, highly functionalized oxindoles[9] and dihydroquinolinones[10] were also obtained by introducing a radical species (Figure 2a). In this case, sulfonylated oxindoles were previously afforded using arylsulfinic acids, sulfonyl hydrazides and sulfonyl chlorides as sulfonyl radical precursors[11] (Figure 2b). In 2015, Wang's group[11a] developed photocatalytic synthesis of sulfonated oxindoles compounds using arylsulfinic acids as the sulfone source, Na_2-Eosin Y as the photocatalyst, and *tert*-butyl hydroperoxide (TBHP) as the oxidant. In 2020, Yu's group[11b] used the Acr^+-Mes•ClO_4^- as the photocatalyst and $K_2S_2O_8$ as the oxidant to construct the oxindoles through the cascade sulfonated cyclization reaction. In 2021, Wang *et al.*[11c] successfully constructed sulfonated oxindoles using sulfonyl chloride as the sulfone source by the action of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 and base. Within our ongoing program on sustainable chemistry,[12] herein, we use the more stable sulfinate salts as the sulfonyl source to construct sulfonylated oxindoles under visible light-induced photocatalyst-free conditions (Figure 2c).

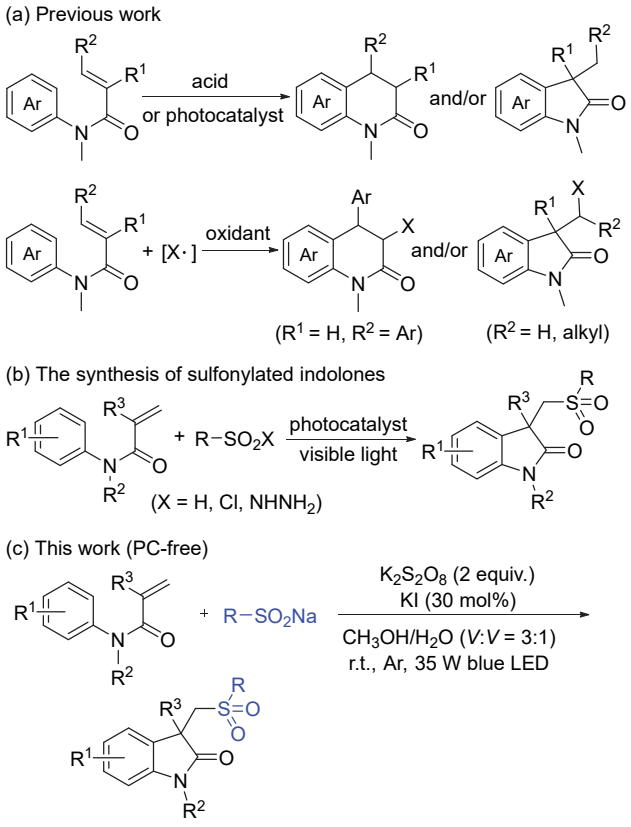


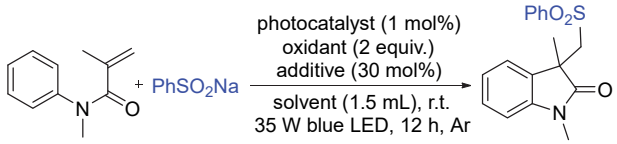
Figure 2 Photocatalytic cyclization of *N*-arylacrylamides

2 Results and discussion

Initially, *N*-methyl-*N*-phenylmethacrylamide (**1a**) and sodium benzene sulfonate (**2a**) were chosen as model substrates for conditional exploration. First, the reaction was carried out by the use of Ir(dF(CF_3)ppy)$_2$(dtbpy)]PF_6 as the photocatalyst, KI as the additive, MeOH as the solvent under 35 W blue LED light irradiation and air atmosphere for 12 h. The target product was produced in 10% yield (Entry 1, Table 1). An oxidant was then added and It was found that the yield increased to 59% with potassium persulfate (Entry 2, Table 1). Other oxidant such as TBHP and di-*tert*-butyl peroxide (DTBP) decreased the yield to 30% and 25%, respectively (Entries 3～4, Table 1). Then other halide additives were optimized including NaI, LiBr, and NaBr, all of which were inferior to KI (Entries 5～7, Table 1). The color of KI-containing reaction mixture changed quickly to brown after combination, which means rapid formation of elemental iodine that probably facilitated the efficiency of reaction. The solvent effect was explored and it was found that yields were reduced with other solvents (Entries 8～11, Table 1). The yield was dramatically declined to 16% in the absence of water (Entry 12, Table 1). When we increased the amount of oxidant to 2 equivalents, the target product was obtained in 89% yield (Entry 13, Table 1). Next, a control experiment was performed. It is gratifying that the yield reached to 90% in the absence of photocatalyst (Entry 14, Table 1). The experimental results show that potassium persulfate is a necessary factor for this reaction; otherwise only small amounts of the target product was detected. And the halide additive could greatly improve the reaction efficiency (Entries 15～16, Table 1). The yield is 39% under dark conditions, and slightly enhanced to 41% under 80 °C heating conditions in the absence of light (Entries 17～18, Table 1). When I_2 was used to replace the combination of KI and $K_2S_2O_8$, the target **3aa** was afforded in 28% yield (Entry 19, Table 1), in which iodization reaction of **1a** at both benzene ring and alkene moieties mainly occurred. The yield decreased to 65% when the reaction was carried out under air (Entry 20, Table 1).

With the optimized conditions in hand, our attention was turned to investigating the substrate scope. The results are summarized in Table 2. The scope of acrylamides with substituents on the benzene ring was first investigated. The *N*-methylarylacrylamides containing both electron-donating and electron-withdrawing groups at the *para*-position of the benzene rings reacted smoothly with sodium benzene sulfonate **2** under standard conditions, affording the corresponding compounds in good to excellent yields (**3aa**～**3ql**, 60%～90%). As expected, *meta*-substituted substrates gave a mixture of two regioselective products (**3am**, 88%). Next, the substrates with various N-protecting groups were exploited. The substrates with benzyl, phenyl, and isopropyl groups were all compatible with the conditions (**3an**～**3ap**), but N—H arylacrylamide did not work at all. When the tetrahydroquinoline derivative was used as

Table 1 Optimization on reaction conditions



1a **2a** **3aa**

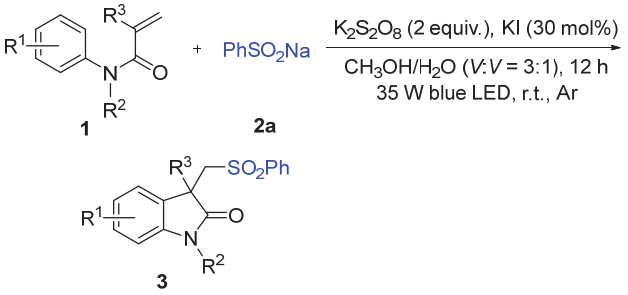
Entry	Photocatalyst	Additive	Oxidant	Aolvent	Yield[a]/%
1	[Ir]PF_6	KI	Air	MeOH	10
2	[Ir]PF_6	KI	$K_2S_2O_8$	MeOH	59
3	[Ir]PF_6	KI	TBHP	MeOH	30
4	[Ir]PF_6	KI	DTBP	MeOH	25
5	[Ir]PF_6	NaI	$K_2S_2O_8$	MeOH	30
6	[Ir]PF_6	LiBr	$K_2S_2O_8$	MeOH	10
7	[Ir]PF_6	NaBr	$K_2S_2O_8$	MeOH	Trace
8	[Ir]PF_6	KI	$K_2S_2O_8$	MeCN	45
9	[Ir]PF_6	KI	$K_2S_2O_8$	DMSO	30
10	[Ir]PF_6	KI	$K_2S_2O_8$	Acetone	27
11	[Ir]PF_6	KI	$K_2S_2O_8$	THF	25
12[b]	[Ir]PF_6	KI	$K_2S_2O_8$	MeOH	16
13[c]	[Ir]PF_6	KI	$K_2S_2O_8$	MeOH	89
14[c]	—	KI	$K_2S_2O_8$	MeOH	90
15[c]	—	—	$K_2S_2O_8$	MeOH	33
16	—	KI	—	MeOH	Trace
17[d]	—	KI	$K_2S_2O_8$	MeOH	39
18[d,e]	—	KI	$K_2S_2O_8$	MeOH	41
19[f]	—	—	—	MeOH	28
20[g]	—	KI	$K_2S_2O_8$	MeOH	65

[a] Reaction conditions: **1** (0.2 mmol), **2** (2.2 equiv), photocatalyst (1 mol%), additive (0.3 equiv.), oxidant (1 equiv.), H_2O (0.5 mL), solvent (1.5 mL), Ar, 35 W blue LED, 12 h, isolated yield was given. [b] Without water. [c] 2 equiv. of oxidant was used. [d] In dark. [e] At 80 °C. [f] I_2 (2 equiv.) replacing KI and $K_2S_2O_8$. [g] Under air atmosphere. [Ir]PF_6 refers to Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6.

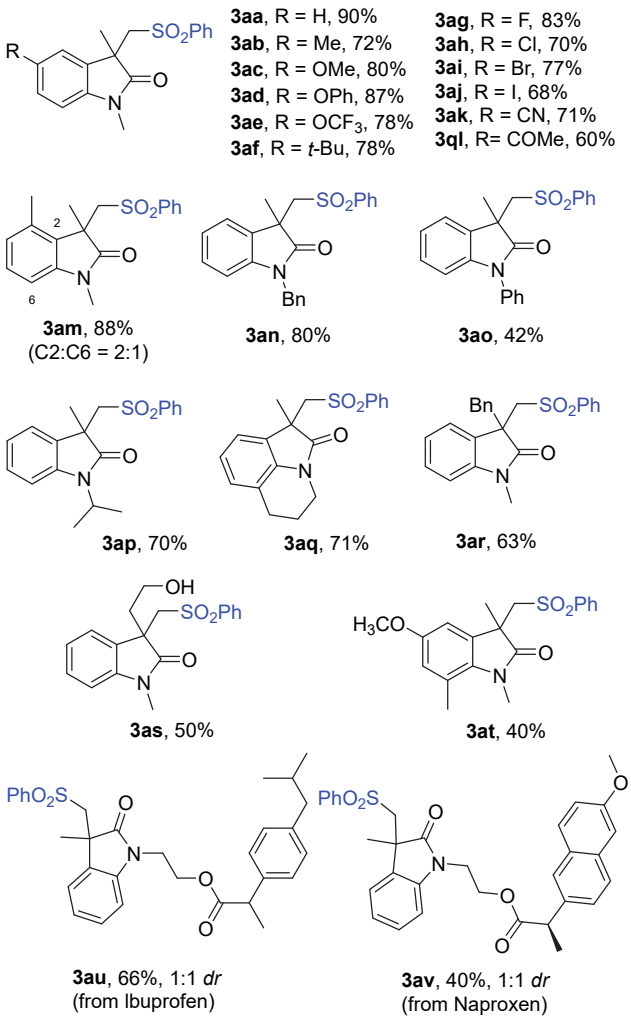
the substrate, the expected product **3aq** was afforded in 71% yield. The *α*-benzyl and hydroxyethyl acrylamides provided the corresponding sulfonylated oxindoles in moderate yields (**3ar**, **3as**). To further demonstrate the robustness and usefulness of this protocol, the photocatalyst-free protocol was applied to the late-stage functionalization of complex molecules. For instance, the molecules with ibuprofen and naproxen moieties were compatible with the reaction and smoothly furnished the desired products **3au** and **3av**, respectively.

Subsequently, different sodium sulfinates were evaluated (Table 3). When the *para*-position of sodium aryl sulfinate was replaced by synthetically useful halogen including F, Cl and Br, they were well tolerated and the corresponding products (**3ba**～**3bc**) were obtained in 73%～81% yields. It was exciting that the strongly electron-withdrawing nitro group could also be tolerated, albeit in a low yield (**3bd**). Various substituted sodium aryl sulfinates bearing methyl, methoxy, and *tert*-butyl groups on the aromatic rings worked efficiently with *N*-methyl-*N*-phenylmethacrylamide and afforded the corresponding sulfonylated oxindoles in good yields (**3be**～**3bg**, 79%～87%).

Table 2 Substrate scope of *N*-arylacrylamide



1 **2a** **3**

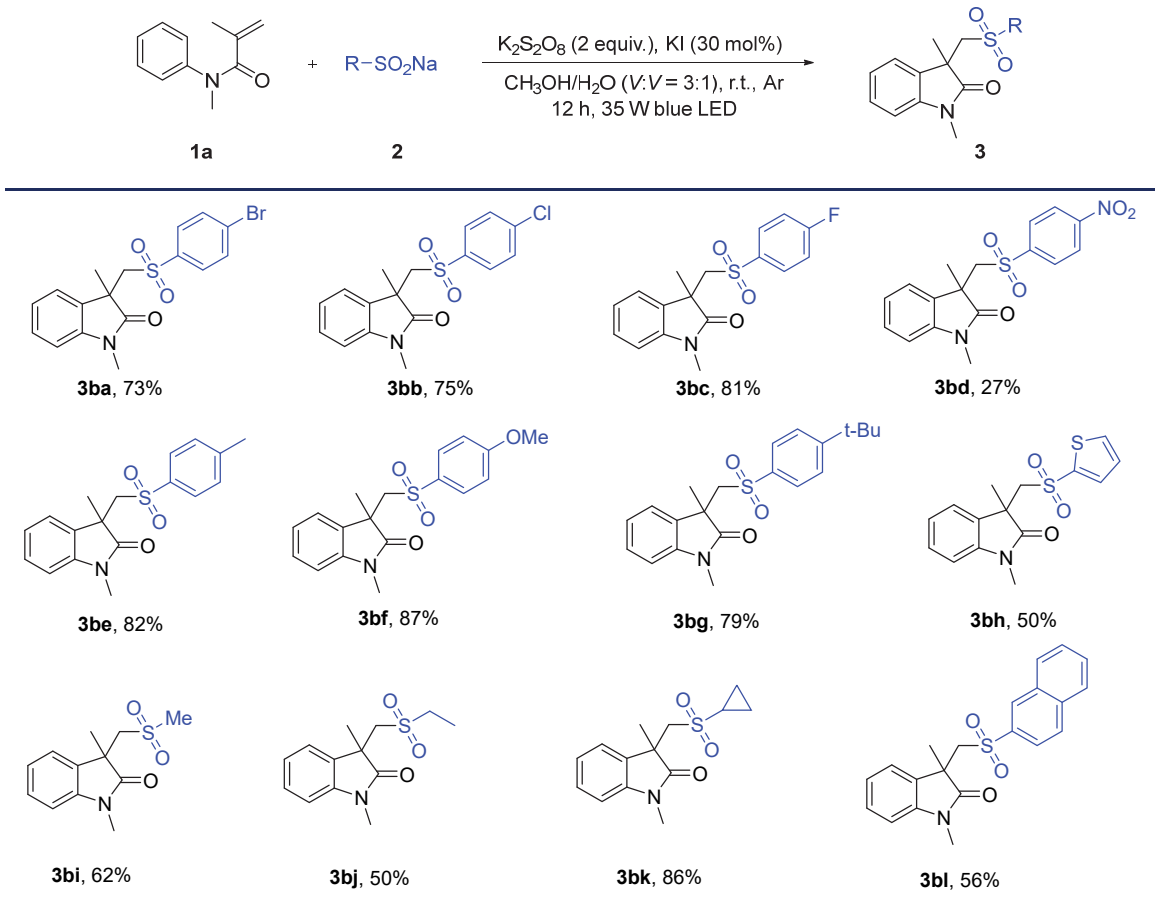


Furthermore, the thiophene ring could also undergo the radical addition/cyclization transformation, providing the expected product **3bh** in 73% yield. To our surprise, both acyclic and cyclic aliphatic sodium sulfinates were compatible with this system (**3bi**～**3bk**, 50%～86%). Finally, the bulky sodium 2-naphthalene sulfinate also reacted efficiently, affording the desired product **3bl** in 56% yield.

The efficient gram-scale preparation further reflects the sustainability value of this reaction, where the target product **3aa** was obtained in 81% yield when **1a** reacted on a 6.0 mmol scale under the standard conditions (Figure 3).

In order to explore the reaction mechanism, the related

Table 3 Substrate scope of sodium sulfinates



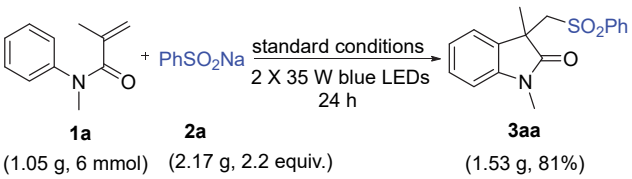


Figure 3 Gram-scale reaction for the synthesis of **3aa**

mechanistic experiments were carried out (Figure 4). First, the light switch on/off experiments were carried out. The results show that the reaction probably includes a free radical chain process (Figure 4a). UV-Vis absorption experiments for **1a**, **2a**, KI, and $K_2S_2O_8$ in solutions with the same concentration as the actual reaction mixture were then performed (Figure 4b). These results show a variety of single components whose absorption occurs only in the UV region (<360 nm). When the combinational KI and $K_2S_2O_8$ were tested, an absorption in the visible region with an onset wavelength of about 550 nm was found. In addition, the UV absorption of iodine was done, which likewise showed an absorption in the visible region. We

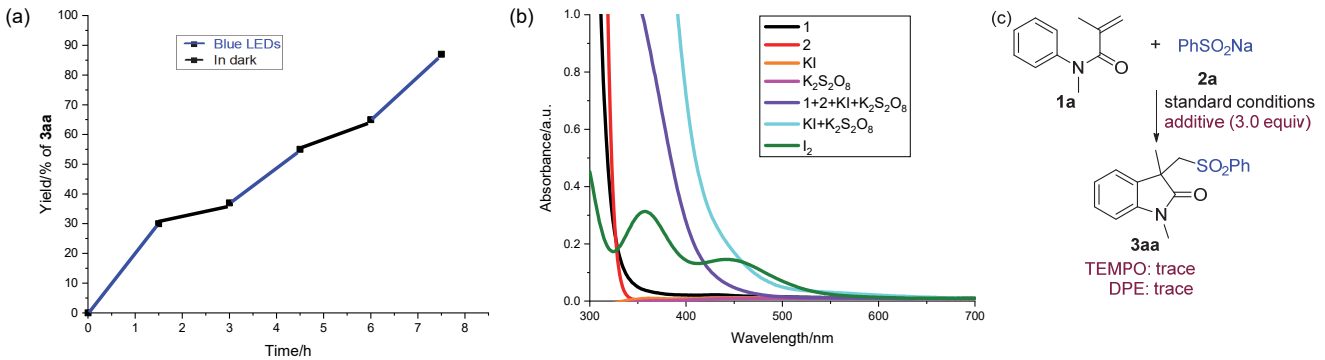


Figure 4 Mechanistic studies

(a) Light on/off experiments; (b) UV-vis absorption spectra of reactants; (c) Radical inhibition experiments

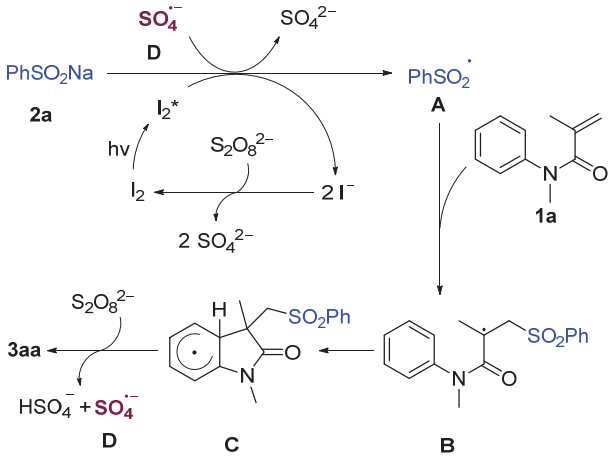


Figure 5 Possible mechanism

speculate that the combination of KI and $K_2S_2O_8$ would *in-situ* form elemental I_2 to absorb photon in the initial step.[13] Finally, the addition of a radical inhibitor such as 2,2,6,6-tetramethylpiperidinooxy (TEMPO) and 1,1-diphenylethylene (DPE) almost completely inhibited the radical addition/cyclization reaction (Figure 4c), in which **1a** was fully recovered and the radical trapping products of sulfonyl radical were not detected.

Based on above studies, a possible reaction mechanism was proposed (Figure 5). First, KI is oxidized by $K_2S_2O_8$ to generate I_2 and sulfate dianion. I_2 generates the excited state I_2* under light irradiation, and sulfinate **2** is oxidized to the radical intermediate **A** by I_2*. Subsequently, intermediate **A** undergoes radical addition to acrylamide **1** to obtain intermediate **B**, with intramolecular cyclization to give intermediate **C**. Intermediate **C** is oxidized by $K_2S_2O_8$ to produce the sulfonylated oxindole **3aa**, sulfate dianion, and sulfate radical anion (**D**). The later is supposed to oxidize sulfinate to enable a radical chain reaction pathway.

3 Conclusions

In conclusion, we have demonstrated a visible-light-assisted cascade sulfonylation/cyclization reaction of *N*-arylacrylamides with sulfonate sodium salts for the construction of various sulfonylated oxindoles. This protocol uses inexpensive oxidant without the requirement for photocatalyst and transition-metal catalyst. It features high reaction efficiency and broad functional group tolerance.

4 Experimental section

4.1 Instruments and reagents

All experiments were carried out in an Ar atmosphere with a 35 W blue LED light as the light source. Unless otherwise specified, all starting materials were purchased commercially and used directly, and the reaction was followed by thin layer chromatography (TLC) to track the progress of the reaction. 200～300 mesh silica gel was used for column chromatography, and GF254 silica gel plate was used for TLC. The test frequencies of ^{1}H NMR and ^{13}C NMR were 400 and 100 MHz, respectively. The chemical shifts were referenced to the signals at δ 0.00 and 77.0, respectively, and TMS was used as the internal standard.

4.2 Experimental method

To a 10 mL glassware equipped with a stir bar were added 0.2 mmol of acrylamide, 0.44 mmol of sodium sulfinate, 0.06 mmol of KI, and 0.4 mmol of $K_2S_2O_8$ dissolved in 1.5 mL of methanol and 0.5 mL of water. The mixture was stirred and irradiated with a 35 W blue LED at room temperature for 12 h. After the reaction, water was added to the reaction solution, and the mixture was extracted with ethyl acetate for three times. The organic phases were combined and dried over anhydrous magnesium sulfate, filtered, and then distilled under reduced pressure. The target product was obtained by column chromatography (V(ethyl acetate)∶V(petroleum ether)＝2∶1～5∶1).

4.3 Characterization data of products

1,3-Dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3aa**): White solid, 90% yield. m.p. 158～160 °C (lit.[14] 159.3～161.9 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.56～7.48 (m, 3H), 7.38 (t, J=7.8 Hz, 2H), 7.30 (dd, J=7.7, 1.0 Hz, 1H), 7.05 (d, J=7.1 Hz, 1H), 6.92～6.83 (m, 2H), 3.89 (d, J=14.6 Hz, 1H), 3.69 (d, J=14.6 Hz, 1H), 3.17 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ: 177.60, 143.22, 139.86, 129.42, 128.88, 128.61, 127.74, 124.02, 108.39, 61.78, 45.58, 26.53, 25.43.

1,3,5-Trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ab**): White solid, 72% yield. m.p. 147～149 °C (lit.[14] 148.8～151.0 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.52 (t, J=7.4 Hz, 1H), 7.41 (d, J=7.8 Hz, 2H), 7.33 (t, J=7.8 Hz, 2H), 7.04 (d, J=7.8 Hz, 1H), 6.74 (d, J=7.9 Hz, 1H), 6.63 (s, 1H), 3.90 (d, J=14.7 Hz, 1H), 3.69 (d, J=14.7 Hz, 1H), 3.18 (s, 3H), 2.11 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ: 177.48, 140.96, 139.87, 133.03, 131.76, 129.21, 128.87, 128.60, 127.65, 124.65, 108.05, 45.50, 26.52, 25.33, 20.81.

5-Methoxy-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ac**): White solid, 80% yield. m.p. 130～132 °C (lit.[14] 129.1～131.4 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.53 (t, J=7.4 Hz, 1H), 7.46 (d, J=7.5 Hz, 2H), 7.36 (t, J=7.8 Hz, 2H), 6.81～6.73 (m, 2H), 6.52 (d, J=2.2 Hz, 1H), 3.89 (d, J=14.7 Hz, 1H), 3.68 (d, J=14.7 Hz, 1H), 3.64 (s, 3H), 3.17 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ: 177.18, 155.68, 139.84, 136.66, 133.20, 130.45, 128.71, 127.68, 113.21, 110.90, 108.69, 61.71, 55.42, 45.92, 26.58, 25.30.

1,3-Dimethyl-5-phenoxy-3-((phenylsulfonyl)methyl)indolin-2-one (**3ad**): White solid, 87% yield. m.p. 147～149 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.62～7.56 (m, 3H), 7.46～7.41 (m, 2H), 7.35～7.29 (m, 2H), 7.07 (t, J=7.4 Hz, 1H), 7.00～6.94 (m, 3H), 6.87 (d, J=2.3 Hz, 1H), 6.81 (d, J=8.4 Hz, 1H), 3.86 (d, J=14.5 Hz, 1H), 3.61 (d, J=14.5 Hz, 1H), 3.17 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ: 177.35, 157.80, 152.23, 139.76,

138.99, 133.54, 130.97, 129.63, 128.90, 127.71, 122.70, 119.53, 117.78, 116.55, 109.01, 61.54, 45.82, 26.61, 25.38. HRMS (ESI) calcd for $C_{23}H_{21}NO_4SNa$ $(M+Na)^+$: 430.1083, found 430.1093.

1,3-Dimethyl-3-((phenylsulfonyl)methyl)-5-(trifluoromethoxy)indolin-2-one (**3ae**): White solid, 78% yield. m.p. 100～102 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.56 (dd, *J*=15.4, 7.9 Hz, 3H), 7.44～7.38 (m, 2H), 7.16 (dd, *J*=7.7, 2.1 Hz, 1H), 6.97～6.94 (m, 1H), 6.85 (d, *J*=8.5 Hz, 1H), 3.87 (d, *J*=14.6 Hz, 1H), 3.70 (d, *J*=14.6 Hz, 1H), 3.20 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.48, 144.60, 141.97, 139.75, 133.75, 131.09, 129.05, 127.64, 121.75, 120.46 (d, *J*=256 Hz), 118.16, 108.87, 61.61, 45.94, 26.77, 25.26; ^{19}F NMR (376 MHz, Chloroform-*d*) *δ*: −58.25. HRMS (ESI) calcd for $C_{18}H_{16}F_3NO_4SNa$ $(M+Na)^+$: 422.0644, found 422.0657.

5-(*tert*-Butyl)-1,3-dimethyl-3-((phenylsulfonyl)methyl)-indolin-2-one (**3af**): Yellow solid, 78% yield. m.p. 56～57 ºC (lit.[14] 55.4～57.3 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.51 (dd, *J*=14.8, 7.4 Hz, 3H), 7.36 (t, *J*=7.8 Hz, 2H), 7.31 (dd, *J*=8.2, 1.8 Hz, 1H), 7.17 (s, 1H), 6.77 (d, *J*=8.2 Hz, 1H), 3.88 (d, *J*=14.6 Hz, 1H), 3.73 (d, *J*=14.6 Hz, 1H), 3.14 (s, 3H), 1.41 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.68, 145.54, 140.74, 139.92, 133.36, 129.03, 128.75, 127.72, 125.27, 121.38, 107.70, 61.84, 45.83, 34.42, 31.45, 26.46, 25.45.

5-Fluoro-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ag**): White solid, 83% yield. m.p. 168～170 ºC (lit.[14] 168.6～169.4 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.60～7.49 (m, 3H), 7.40 (t, *J*=7.8 Hz, 2H), 6.97 (td, *J*=8.9, 2.5 Hz, 1H), 6.78 (dd, *J*=8.5, 4.1 Hz, 1H), 6.72 (dd, *J*=7.9, 2.5 Hz, 1H), 3.88 (d, *J*=14.7 Hz, 1H), 3.69 (d, *J*=14.7 Hz, 1H), 3.19 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.21, 158.88 (d, *J*=239 Hz), 139.66, 139.16 (d, *J*=2 Hz), 133.50, 130.95 (d, *J*=8 Hz), 128.88, 127.55, 114.90 (d, *J*=23 Hz), 112.13 (d, *J*=25 Hz), 108.80 (d, *J*=8 Hz), 61.47, 45.90, 26.63, 25.15.

5-Chloro-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ah**): White solid, 70% yield. m.p. 146～148 ºC (lit.[14] 147.6～148.9 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.58 (t, *J*=7.3 Hz, 1H), 7.49～7.44 (m, 2H), 7.39 (t, *J*=7.8 Hz, 2H), 7.22 (dd, *J*=8.4, 2.0 Hz, 1H), 6.81～6.77 (m, 2H), 3.90 (d, *J*=14.7 Hz, 1H), 3.69 (d, *J*=14.7 Hz, 1H), 3.21 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.12, 141.94, 139.56, 133.60, 130.91, 128.87, 128.59, 127.73, 127.47, 124.37, 109.30, 61.56, 45.65, 26.67, 25.16.

5-Bromo-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ai**): Yellow solid, 77% yield. m.p. 162～164 ºC (lit.[14] 161.8～163.1 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.59 (t, *J*=7.2 Hz, 1H), 7.45 (d, *J*=7.7 Hz, 2H), 7.42～7.34 (m, 3H), 6.90 (d, *J*=1.2 Hz, 1H), 6.75 (d, *J*=8.3 Hz, 1H), 3.90 (d, *J*=14.8 Hz, 1H), 3.68 (d, *J*=14.8 Hz, 1H), 3.22 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.03, 142.47, 139.53, 133.69, 131.49, 131.27, 128.90, 127.46, 127.07, 115.10, 109.83, 61.61, 45.61, 26.68, 25.19.

5-Iodo-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3aj**): White solid, 68% yield. m.p. 175～177 ºC (lit.[14] 173.0～174.6 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.63-7.59 (m, 1H), 7.56～7.52 (m, 1H), 7.45～7.36 (m, 4H), 7.02 (d, *J*=1.3 Hz, 1H), 6.66 (d, *J*=8.2 Hz, 1H), 3.89 (d, *J*=14.8 Hz, 1H), 3.68 (d, *J*=14.8 Hz, 1H), 3.21 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHZ, Chloroform-*d*) *δ*: 176.83, 143.14, 139.42, 137.34, 133.77, 132.48, 131.51, 128.88, 127.37, 110.41, 85.13, 61.58, 45.38, 26.60, 25.15.

1,3-Dimethyl-2-oxo-3-((phenylsulfonyl)methyl)indoline-5-carbonitrile (**3ak**): White solid, 71% yield. m.p. 173～175 ºC (lit.[14] 173.1～175.4 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.66～7.57 (m, 2H), 7.50 (d, *J*=7.4 Hz, 2H), 7.44 (t, *J*=7.7 Hz, 2H), 7.12 (s, 1H), 6.96 (d, *J*=8.2 Hz, 1H), 3.91 (d, *J*=14.7 Hz, 1H), 3.75 (d, *J*=14.7 Hz, 1H), 3.28 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.45, 147.24, 139.58, 133.84, 133.79, 130.42, 129.11, 127.38, 127.25, 118.69, 108.90, 105.60, 61.42, 45.24, 26.83, 24.99.

5-Acetyl-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3al**): White solid, 60% yield. m.p. 182～184 ºC (lit.[15] 183.2 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.92 (dd, *J*=8.2, 1.6 Hz, 1H), 7.51～7.41 (m, 4H), 7.34 (t, *J*=7.8 Hz, 2H), 6.93 (d, *J*=8.2 Hz, 1H), 3.94 (d, *J*=14.7 Hz, 1H), 3.80 (d, *J*=14.7 Hz, 1H), 3.29 (s, 3H), 2.45 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 196.16, 177.99, 147.70, 139.78, 133.25, 131.77, 130.38, 129.38, 128.87, 127.37, 123.78, 107.92, 61.62, 45.22, 26.81, 26.23, 25.09.

1,3,4-Trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3am**) and 1,3,6-trimethyl-3-((phenylsulfonyl)methyl)-indolin-2-one (**3am'**) (2∶1):[15] Colorless oil, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.57～7.48 (m, 3H), 7.45～7.32 (m, 6H), 7.20 (t, *J*=7.8 Hz, 1H), 6.92 (d, *J*=7.5 Hz, 1H), 6.73～6.64 (m, 3H), 3.98 (d, *J*=14.7 Hz, 1H), 3.86 (d, *J*=3.8 Hz, 1H), 3.83 (d, *J*=4.0 Hz, 1H), 3.67 (d, *J*=14.5 Hz, 1H), 3.15 (s, 2H), 3.14 (s, 3H), 2.38 (s, 2H), 2.06 (s, 3H), 1.40 (s, 3H), 1.37 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.86, 177.57, 143.63, 143.21, 139.93, 139.33, 138.72, 135.30, 133.33, 133.22, 128.75, 128.69, 128.58, 128.02, 127.67, 126.49, 124.96, 123.68, 123.01, 109.23, 106.11, 61.87, 60.80, 45.80, 45.32, 26.55, 26.43, 25.35, 23.09, 21.76, 18.07.

1-Benzyl-3-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3an**): White solid, 80% yield. m.p. 160～162 ºC (lit.[16] 162～163 ºC); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.54～7.49 (m, 3H), 7.39～7.29 (m, 6H), 7.25 (t, *J*=7.1 Hz, 1H), 7.14～7.08 (m, 1H), 6.97 (d, *J*=7.4 Hz, 1H), 6.79 (t, *J*=7.4 Hz, 1H), 6.70 (d, *J*=7.8 Hz, 1H), 5.00 (d, *J*=15.8 Hz, 1H), 4.80 (d, *J*=15.8 Hz, 1H), 3.94 (d, *J*=14.6 Hz, 1H), 3.76 (d, *J*=14.6 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.73, 142.25, 139.90, 135.67, 133.29, 129.35, 128.87, 128.67, 128.35, 127.63, 127.51, 127.23, 123.79, 122.45, 109.47, 61.47, 45.62, 44.13, 25.93.

3-Methyl-1-phenyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ao**): White solid, 42% yield. m.p. 151～153 °C (lit.[17] 153～154 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.56～7.49 (m, 7H), 7.46-7.42 (m, 1H), 7.36 (t, *J*=7.8 Hz, 2H), 7.20～7.15 (m, 1H), 6.98～6.93 (m, 1H), 6.87～6.80 (m, 2H), 4.00 (d, *J*=14.6 Hz, 1H), 3.79 (d, *J*=14.6 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.33, 143.54, 140.22, 134.44, 133.24, 129.59, 129.21, 128.99, 128.46, 128.19, 127.51, 126.82, 123.80, 122.82, 109.67, 62.27, 45.67, 25.62.

1-Isopropyl-3-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ap**): Light yellow solid, 70% yield. m.p. 179～181 °C (lit.[18] 181～184 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.52-7.48 (m, 3H), 7.35 (t, *J*=7.8 Hz, 2H), 7.23～7.18 (m, 1H), 7.05 (d, *J*=7.9 Hz, 1H), 6.88 (d, *J*=7.1 Hz, 1H), 6.75 (t, *J*=7.5 Hz, 1H), 4.74～4.65 (m, 1H), 3.86 (d, *J*=14.6 Hz, 1H), 3.68 (d, *J*=14.6 Hz, 1H), 1.56 (d, *J*=7.0 Hz, 3H), 1.52 (d, *J*=7.0 Hz, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.31, 141.92, 140.28, 133.11, 129.79, 128.89, 128.13, 127.40, 123.81, 121.79, 110.13, 61.83, 45.26, 43.93, 25.50, 19.30, 18.78.

1-Methyl-1-((phenylsulfonyl)methyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-2(1*H*)-one(**3aq**): White solid, 71% yield. m.p. 144～146 °C (lit.[19] 145～146 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.54 (t, *J*=7.6 Hz, 3H), 7.39 (t, J=8.4 Hz, 2H), 7.03 (d, *J*=7.6 Hz, 1H), 6.91 (d, *J*=7.4 Hz, 1H), 6.80 (t, *J*=7.6 Hz, 1H), 3.85 (d, *J*=14.5 Hz, 1H), 3.74～3.59 (m, 3H), 2.79 (q, *J*=5.3 Hz, 2H), 2.07～1.95 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 176.42, 139.93, 138.93, 133.29, 128.85, 128.03, 127.68, 127.26, 121.94, 121.87, 120.38, 61.70, 46.71, 39.01, 24.98, 24.48, 20.92.

3-Benzyl-1-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3ar**): White solid, 63% yield. m.p. 163～165 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.55～7.46 (m, 3H), 7.36 (t, *J*=7.8 Hz, 2H), 7.23～7.17 (m, 1H), 7.11～7.07 (m, 1H), 7.03 (t, *J*=7.2 Hz, 2H), 6.96 (d, *J*=6.9 Hz, 1H), 6.88 (t, *J*=7.5 Hz, 1H), 6.72 (d, *J*=7.0 Hz, 2H), 6.57 (d, *J*=7.8 Hz, 1H), 4.05 (d, *J*=14.5 Hz, 1H), 3.81 (d, *J*=14.5 Hz, 1H), 3.00 (s, 2H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 176.17, 143.71, 139.81, 133.34, 130.03, 128.79, 128.67, 127.82, 127.51, 127.02, 126.48, 125.13, 121.94, 108.01, 60.72, 50.94, 44.70, 26.06. HRMS (ESI) calcd for $C_{23}H_{21}NO_3SNa$ $(M+Na)^+$: 414.1134, found 414.1144.

3-(2-Hydroxyethyl)-1-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3as**): White solid, 50% yield. m.p. 113～115 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.53 (t, *J*=7.4 Hz, 1H), 7.48～7.43 (m, 2H), 7.36 (t, *J*=7.8 Hz, 2H), 7.31～7.24 (m, 1H), 6.97 (d, *J*=7.2 Hz, 1H), 6.86 (t, *J*=7.0 Hz, 2H), 3.95 (d, *J*=14.7 Hz, 1H), 3.86 (d, *J*=14.7 Hz, 1H), 3.52～3.37 (m, 2H), 3.18 (s, 3H), 2.19 (s, 1H), 2.04 (qt, *J*=14.0, 6.2 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.59, 143.70, 139.94, 133.29, 128.89, 128.84, 127.55, 127.27, 122.59, 108.53, 58.00, 48.18, 40.64. HRMS (ESI) calcd for $C_{18}H_{19}NO_4SNa$ $(M+Na)^+$: 368.0927, found 368.0938.

5-Methoxy-1,3,7-trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (**3at**): White solid, 40% yield. m.p. 148～150 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.56～7.50 (m, 1H), 7.49-7.46 (m, 2H), 7.40～7.33 (m, 2H), 6.52 (d, *J*=2.2 Hz, 1H), 6.33 (d, *J*=2.5 Hz, 1H), 3.90 (d, *J*=14.6 Hz, 1H), 3.64 (d, *J*=14.7 Hz, 1H), 3.61 (s, 3H), 3.42 (s, 3H), 2.55 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 178.08, 155.14, 139.92, 134.50, 133.17, 131.11, 128.66, 127.82, 120.95, 117.23, 107.96, 62.08, 55.28, 45.47, 29.91, 25.79, 19.02. HRMS (ESI) calcd for $C_{19}H_{21}NO_4SNa$ $(M+Na)^+$: 382.1038, found 382.1094.

2-(3-Methyl-2-oxo-3-((phenylsulfonyl)methyl)indolin-1-yl)ethyl 2-(4-isobutylphenyl)propanoate (**3au**, *dr* = 1∶1): White solid, 66% yield. m.p. 150～152 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.54～7.44 (m, 3H), 7.38-7.32 (m, 2H), 7.24～7.17 (m, 1H), 7.14-7.08 (m, 2H), 7.06-7.02 (m, 2H), 6.94 (t, *J*=6.5 Hz, 1H), 6.89-6.80 (m, 2H), 4.44～4.23 (m, 2H), 4.00～3.76 (m, 3H), 3.72～3.58 (m, 2H), 2.42 (d, *J*=7.1 Hz, 2H), 1.88-1.77 (m, 1H), 1.40 (dd, *J*=12.3, 7.2 Hz, 3H), 1.32 (d, *J*=10.7 Hz, 3H), 0.88 (d, *J*=6.6 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.68, 177.67, 174.55, 174.53, 142.50, 142.39, 140.50, 140.45, 139.97, 139.89, 137.29, 133.24, 129.26, 129.23, 129.18, 128.84, 128.46, 128.44, 127.57, 127.55, 127.05, 123.91, 123.81, 122.46, 122.42, 108.86, 108.73, 61.75, 61.71, 61.51, 61.33, 45.38, 45.36, 44.95, 44.92, 44.87, 38.99, 30.06, 25.36, 25.28, 22.31, 18.30. HRMS (ESI) calcd for $C_{31}H_{35}NO_5SNa$ $(M+Na)^+$: 556.2128, found 556.2140.

2-(3-Methyl-2-oxo-3-((phenylsulfonyl)methyl)indolin-1-yl)ethyl (2*R*)-2-(6-methoxynaphthalen-2-yl)propanoate (**3av**, *dr*=1∶1): Colorless oil, 40% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.67～7.57 (m, 3H), 7.54～7.43 (m, 3H), 7.37～7.26 (m, 3H), 7.16～7.04 (m, 3H), 6.94～6.88 (m, 1H), 6.83～6.75 (m, 2H), 4.46～4.23 (m, 2H), 3.99～3.84 (m, 5H), 3.84～3.62 (m, 3H), 1.51～1.46 (m, 3H), 1.28 (s, 2H), 1.21 (s, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.73, 177.70, 174.50, 157.57, 157.56, 142.50, 142.37, 140.00, 139.92, 135.26, 135.22, 133.63, 133.61, 133.25, 129.22, 129.17, 128.86, 128.81, 128.79, 128.43, 128.37, 127.59, 127.14, 127.10, 126.07, 126.02, 125.91, 123.93, 123.83, 122.45, 122.40, 118.91, 118.86, 61.71, 61.50, 55.25, 45.39, 45.35, 45.29, 45.23, 39.07, 25.29, 25.21, 18.32, 18.27. HRMS (ESI) calcd for $C_{32}H_{31}NO_6SNa$ $(M+Na)^+$: 580.1764, found 580.1776

3-(((4-Bromophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (**3ba**): White solid, 73% yield. m.p. 170～172 °C (lit.[15] 173～174 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.49 (d, *J*=8.5 Hz, 2H), 7.32～7.27 (m, 3H), 6.98 (d, *J*=7.2 Hz, 1H), 6.90 (t, *J*=7.5 Hz, 1H), 6.85 (d, *J*=7.8 Hz, 1H), 3.91 (d, *J*=14.7 Hz, 1H), 3.70 (d, *J*=14.7 Hz, 1H), 3.17 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.37, 143.18, 138.56, 132.04, 129.28, 129.09, 128.68, 128.66, 123.84, 122.49, 108.42, 61.79, 45.45, 26.50, 25.48.

3-(((4-Chlorophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (**3bb**): White solid, 75% yield. m.p. 179～181 °C

(lit.[15] 180～181 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.37 (d, *J*=8.6 Hz, 2H), 7.34～7.29 (m, 3H), 6.98 (d, *J*=7.1 Hz, 1H), 6.92～6.84 (m, 2H), 3.91 (d, *J*=14.7 Hz, 1H), 3.70 (d, *J*=14.7 Hz, 1H), 3.18 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.39, 143.18, 140.01, 138.07, 129.21, 129.11, 129.05, 128.68, 123.83, 122.46, 108.42, 61.81, 45.46, 26.49, 25.45.

3-(((4-Fluorophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (**3bc**): White solid, 81% yield. m.p. 154～156 °C (lit.[15] 156～157 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.46 (m, 2H), 7.32～7.26 (m, 1H), 7.06～6.96 (m, 3H), 6.89 (dd, *J*=16.4, 7.8 Hz, 2H), 3.91 (d, *J*=14.7 Hz, 1H), 3.71 (d, *J*=14.7 Hz, 1H), 3.19 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.44, 165.44 (d, *J*=256 Hz), 143.22, 135.84 (d, *J*=3 Hz), 130.62 (d, *J*=9 Hz), 129.25, 128.66, 123.85, 122.46, 116.06 (d, *J*=23 Hz), 108.41, 61.92, 45.51, 26.49, 25.44.

1,3-Dimethyl-3-(((4-nitrophenyl)sulfonyl)methyl)indolin-2-one (**3bd**): Yellow solid, 27% yield. m.p. 194～196 °C (lit.[17] 195～196 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 8.19 (d, *J*=8.8 Hz, 2H), 7.64 (d, *J*=8.8 Hz, 2H), 7.34～7.29 (m, 1H), 6.92～6.86 (m, 2H), 6.82 (t, *J*=7.5 Hz, 1H), 3.98 (d, *J*=14.8 Hz, 1H), 3.75 (d, *J*=14.8 Hz, 1H), 3.23 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.24, 150.42, 145.40, 143.46, 129.20, 129.08, 129.03, 123.96, 123.64, 122.50, 108.66, 62.03, 45.51, 26.63, 25.36.

1,3-Dimethyl-3-(tosylmethyl)indolin-2-one (**3be**): White solid, 82% yield. m.p. 131～133 °C (lit.[17] 132～134 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.34 (d, *J*=8.2 Hz, 2H), 7.29～7.23 (m, 1H), 7.14 (d, *J*=8.1 Hz, 2H), 7.04 (d, *J*=7.3 Hz, 1H), 6.89 (t, *J*=7.5 Hz, 1H), 6.83 (d, *J*=7.8 Hz, 1H), 3.84 (d, *J*=14.5 Hz, 1H), 3.65 (d, *J*=14.5 Hz, 1H), 3.14 (s, 3H), 2.37 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.56, 144.24, 143.12, 136.81, 129.39, 128.47, 127.71, 123.99, 122.36, 108.29, 61.75, 45.52, 26.43, 25.39, 21.48.

3-(((4-Methoxyphenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (**3bf**): White solid, 87% yield. m.p. 147～149 °C (lit.[19] 148～150 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.38 (d, *J*=8.9 Hz, 2H), 7.31～7.25 (m, 1H), 7.06 (d, *J*=7.3 Hz, 1H), 6.96～6.90 (m, 1H), 6.86～6.80 (m, 3H), 3.87 (d, *J*=14.6 Hz, 1H), 3.84 (s, 3H), 3.67 (d, *J*=14.6 Hz, 1H), 3.16 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.58, 163.33, 143.09, 131.23, 129.91, 129.43, 128.47, 123.99, 122.40, 113.93, 108.29, 61.88, 55.58, 45.53, 26.44, 25.46.

3-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (**3bg**): White solid, 79% yield. m.p. 146～148 °C (lit.[20] 147 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.38 (q, *J*=8.7 Hz, 4H), 7.29～7.24 (m, 1H), 7.02 (d, *J*=7.2 Hz, 1H), 6.89～6.83 (m, 2H), 3.87 (d, *J*=14.5 Hz, 1H), 3.68 (d, *J*=14.5 Hz, 1H), 3.17 (s, 3H), 1.39 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.61, 157.09, 143.15, 136.74, 129.43, 128.47, 127.51, 125.84, 123.96, 122.41, 108.30, 61.75, 45.53, 35.08, 30.96, 26.48, 25.39.

1,3-Dimethyl-3-((naphthalen-2-ylsulfonyl)methyl)indolin-2-one (**3bh**): White solid, 56% yield. m.p. 186～188 °C (lit.[17] 187～188 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.87 (dd, *J*=8.2, 3.9 Hz, 2H), 7.81 (s, 1H), 7.75 (d, *J*=8.1 Hz, 1H), 7.68～7.62 (m, 1H), 7.62～7.55 (m, 2H), 7.28～7.17 (m, 1H), 7.00 (d, *J*=7.3 Hz, 1H), 6.80～6.70 (m, 2H), 3.99 (d, *J*=14.6 Hz, 1H), 3.76 (d, *J*=14.7 Hz, 1H), 2.98 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.52, 143.20, 136.32, 135.13, 131.81, 129.96, 129.84, 129.53, 129.22, 129.15, 128.66, 127.81, 127.40, 124.16, 122.57, 122.36, 108.32, 61.60, 45.59, 26.33, 25.69.

1,3-Dimethyl-3-((methylsulfonyl)methyl)indolin-2-one (**3bi**): White solid, 62% yield. m.p. 114～116 °C (lit.[14] 116.0～117.5 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.39～7.31 (m, 2H), 7.12 (t, *J*=7.3 Hz, 1H), 6.92 (d, *J*=8.1 Hz, 1H), 3.72 (d, *J*=14.7 Hz, 1H), 3.59 (d, *J*=14.8 Hz, 1H), 3.27 (s, 3H), 2.61 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.67, 143.34, 130.00, 129.06, 123.44, 122.60, 108.85, 60.72, 45.55, 43.20, 26.56, 24.89.

3-((Ethylsulfonyl)methyl)-1,3-dimethylindolin-2-one (**3bj**):[14] Colorless oil, 50% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.39～7.32 (m, 2H), 7.11 (t, *J*=7.5 Hz, 1H), 6.91 (d, *J*=7.8 Hz, 1H), 3.64 (d, *J*=14.5 Hz, 1H), 3.53 (d, *J*=14.5 Hz, 1H), 3.26 (s, 3H), 2.77-2.66 (m, 2H), 1.46 (s, 3H), 1.27 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.89, 143.25, 130.24, 128.94, 123.43, 122.54, 108.73, 57.68, 49.45, 45.38, 26.56, 24.99, 6.36.

3-((Cyclopropylsulfonyl)methyl)-1,3-dimethylindolin-2-one (**3bk**):[14] Colorless oil, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.40～7.31 (m, 2H), 7.12-7.07 (m, 1H), 6.91 (d, *J*=7.8 Hz, 1H), 3.77 (d, *J*=14.5 Hz, 1H), 3.62 (d, *J*=14.5 Hz, 1H), 3.27 (s, 3H), 2.01～1.92 (m, 1H), 1.46 (s, 3H), 1.12～0.97 (m, 2H), 0.88～0.82 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.90, 143.23, 130.27, 128.88, 123.71, 122.39, 108.66, 59.78, 45.42, 31.39, 26.53, 25.03, 5.12, 5.08.

1,3-Dimethyl-3-((thiophen-2-ylsulfonyl)methyl)indolin-2-one (**3bl**): White solid, 50% yield. m.p. 126～128 °C (lit.[19] 125～127 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) *δ*: 7.59 (dd, *J*=4.9, 1.1 Hz, 1H), 7.32～7.26 (m, 1H), 7.15 (dd, *J*=3.7, 1.2 Hz, 1H), 7.10 (d, *J*=7.4 Hz, 1H), 6.97～6.91 (m, 2H), 6.88 (d, *J*=7.8 Hz, 1H), 3.97 (d, *J*=14.6 Hz, 1H), 3.80 (d, *J*=14.6 Hz, 1H), 3.22 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 177.46, 143.23, 141.02, 134.03, 133.95, 129.38, 128.64, 127.51, 123.85, 122.54, 108.44, 63.23, 45.70, 26.56, 25.29.

Supporting Information UV-Vis absorption spectroscopic measurements. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of all products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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