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光催化氧化交叉偶联制备对称/不对称硫代磺酸酯

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摘要 由于其清洁绿色等特点, 光催化合成已成为国际化学研究的前沿. 报道了一种以硫醇为原料、selectfluor 为氧化剂, eosin Y 为光催化剂, 在蓝光光照下构建 S—S(O)$_2$ 键的方法. 该方法具有条件温和, 官能团兼容性良好, 各种硫醇都能以较好的转化率转化成相应的硫代磺酸酯等优点, 可为开发条件温和、原子经济性高、普适性强的催化体系以实现含硫有机物高效且可控转化提供了非常有价值的参考.

关键词 硫醇; 光催化; 氧化偶联; 硫代磺酸酯

Photocatalyzed Oxidative Cross-Coupling Reaction to Access Symmetrical/Unsymmetrical Thiosulfonates

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Abstract Photocatalysis has become the forefront of international chemical research due to its green and environmentally friendly characteristics. A new protocol to construct S—S(O)$_2$ bonds using selectfluor as oxidant and eosin Y as photocatalyst under blue light irradiation was reported. This method has advantages of mild conditions, good compatibility of functional groups, and easily preparation of various symmetric or asymmetric thiosulfonates various from the corresponding mercaptans with good conversion rates. Thus, this protocol provides a very valuable reference for developing a catalytic system with mild conditions, high atomic economy and strong universality to achieve efficient and controllable conversion of sulfur-containing organic compounds.

Keywords thiol; photocatalysis; oxidative coupling; thiosulfonate

1 Introduction

Organosulfur compounds are ubiquitous in petroleum, animals and plants. They have important applications in medicine, agricultural chemistry and materials science due to their strong physiological activity and unique functions.[1-4] Among them, thiosulfonates have shown a broad spectrum of pharmaceutical and clinical properties[5] such as bactericidal, antiviral and physiological activities.[6] In addition, thiosulfonates have been widely used as reagents or intermediates in laboratory and industrial organic synthesis because they could be employed as the precursors of nucleophiles, electrophiles and free radicals in organic reactions.[7] However, the traditional synthesis method from disulfides, thiols, sulfonyl halides, sulfinate salts or sulfonyl hydrazides does not meet the requirements of green chemistry.[5] Therefore, considerable efforts have been made by chemists in the development new synthetic method for thiosulfonates.

The direct oxidation of disulfides or thiols has been proved to be an efficient approach to synthesize thiosulfonates[8] (Scheme 1, a). In 2016, Xu and coworkers[9] reported a reductive coupling reaction for the synthesis of thiosulfonates and disulfides from sulfonyl chlorides in the presence of tetrabutylammonium iodide (Scheme 1, b). Recently, it has also been reported that thiosulfonates were prepared by decomposition of sulfonyl hydrazine[10] (Scheme 1, c). In the meantime, the unsymmetrical thiosulfonates were usually synthesized by the oxidative coupling of alkali metal sulfinates (Scheme 1, d). For example, in 2012, Wu *et al.*[11a] reported the first example of Sc(OTf)$_3$-catalyzed sulfenylation of sodium sulfifinates

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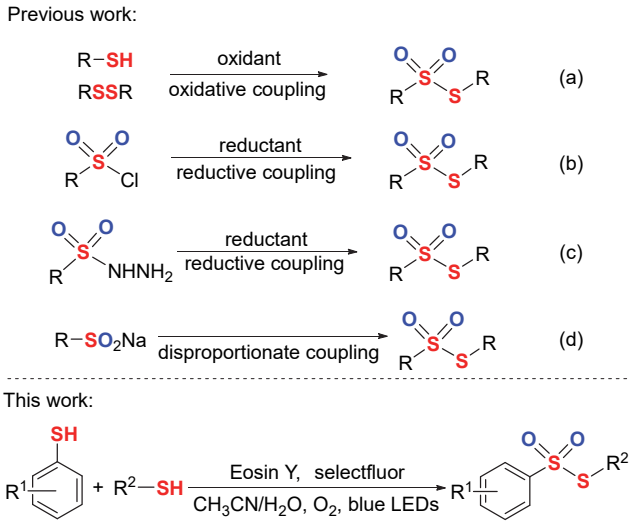
with *N*-(organothio)succinimides in ionic liquids (ILs) and water co-solvent system, achieving thiosulfonates in moderate to excellent yields. Moreover, Wang's group[11b] reported an approach of synthesizing symmetric and asymmetric thiosulfonates via a sulfifinyl radical disproportionation of sodium sulfite mediated by BF_3•OEt_2. However, all the above methods for the synthesis of symmetrical/unsymmetrical thiosulfonates still require the employment of volatile organic solvents or strong oxidants in the harsh conditions. Therefore, the development of more environmentally friendly and metal-free reaction systems to achieve thiosulfonates is still necessary.



Scheme 1 Strategy for the synthesis of thiosulfonates

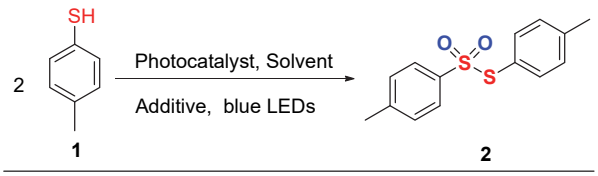
Photocatalysis has become a powerful tool in organic synthesis because of many advantages, such as mild reaction conditions, broad substrates and low consumption. For example, in 2019, Lang and co-works[12] reported a photocatalyzed selectively aerobic oxidation of thiols to disulfides with the assistance of 2,2,6,6-tetramethylpiperidinooxy (TEMPO). Lang's group[13] also reported a selectively aerobic oxidation of sulfides using the combination of polyimide-titanium dioxide photocatalysis and triethylamine catalysis. Furthermore, Li and co-worker[14] demonstrated a radical-involved decarboxylative sulfonylation of sulfinates. The visible-light-induced reaction of redox-active esters of aliphatic carboxylic acids with sulfinates proceeded at room temperature using 4CzIPN and $Cu(OTf)_2$ as catalysts, providing the corresponding decarboxylative sulfonylation products.

To our knowledge, there are no report on the synthesis of thiosulfonates by photocatalysis until now. Herein, we managed to combine the photocatalysis with oxidative cross coupling of thiols to prepare symmetrical and unsymmetrical thiosulfonates by a visible-light-induced and selectfluor-promoted strategy.

2 Results and discussion

The oxidative cross coupling of 4-methylthiophenol was first selected as the model reaction for screening various reaction parameters. The reaction was made up in 3 mL of CH_3CN under O_2 with the irradiation of 18 W blue LEDs at room temperature. When the reaction was conducted in the presence of 9-mesityl-10-methylacridinium perchlorate (5.0 mol%) and selectfluor (2.0 equiv.), the target product was obtained in 77% yield (Table 1, Entry 4). Subsequently, various catalysts (Table 1, Entries 1～5) including 9-fluorenone, 5-carboxyfluorescein, acid red 94 and eosin Y were then investigated for this transformation, and the results showed that eosin Y is the bestl catalyst for this transformation. To obtain the optimal conditions, the effect of oxidants, solvents, the amounts of photocatalysts and oxidants was further investigated. As shown in Table 1 (Entries 1, 6～8), the yield was up to 87% when selectfluor was chosen as the oxidant (Entry 1). In this reaction, the mixed solvent of H_2O and CH_3CN could give the best yield in comparison with H_2O, CH_3CN, EtOH, dichloro-

Table 1 Optimization of reaction conditions[a,b]



Eosin Y PC-1 | 9-fluorenone PC-2 | Acid Red 94 PC-3

9-mesityl-10-methylacridinium perchlorate PC-4 | 5-arboxyfluorescein PC-5

Entry	Catalyst	Oxidant	Solvent	Yield[b]/%
1	PC-1	selectfluor	CH_3CN	87
2	PC-2	selectfluor	CH_3CN	50
3	PC-3	selectfluor	CH_3CN	72
4	PC-4	selectfluor	CH_3CN	77
5	PC-5	selectfluor	CH_3CN	64
6	PC-1	CH_3CO_3H	CH_3CN	63
7	PC-1	TBPO	CH_3CN	74
8	PC-1	H_2O_2	CH_3CN	Trace
9	PC-1	selectfluor	H_2O	82
10	PC-1	selectfluor	EtOH	42
11	PC-1	selectfluor	DCM	17
12[c]	PC-1	selectfluor	CH_3CN/H_2O	89
13[c]	—	selectfluor	CH_3CN/H_2O	Trace
14[c]	PC-1	—	CH_3CN/H_2O	34
15[c,d]	PC-1	selectfluor	CH_3CN/H_2O	64
16[c,e]	PC-1	selectfluor	CH_3CN/H_2O	90
17[c,f]	PC-1	selectfluor	CH_3CN/H_2O	78
18[c,g]	PC-1	selectfluor	CH_3CN/H_2O	92
19[c,h]	PC-1	selectfluor	CH_3CN/H_2O	58
20[c,i]	PC-1	selectfluor	CH_3CN/H_2O	78
21[c,j]	PC-1	selectfluor	CH_3CN/H_2O	77

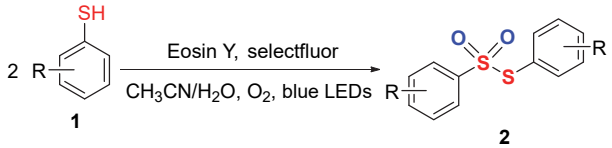
[a] Reaction conditions: **1** (0.5 mmol), photocatalyst (5.0 mol%), oxidant (2.0 equiv.), solvent (3.0 mL), room temperature, 6 h, O_2; [b] isolated yields. [c] CH_3CN/H_2O (3 mL, V∶V=1∶1); [d] oxidant (1.2 equiv.); [e] oxidant (3.0 equiv.); [f] photocatalyst (3.0 mol%); [g] photocatalyst (10.0 mol%); [h] under natural light; [i] under air. [j] 3 h.

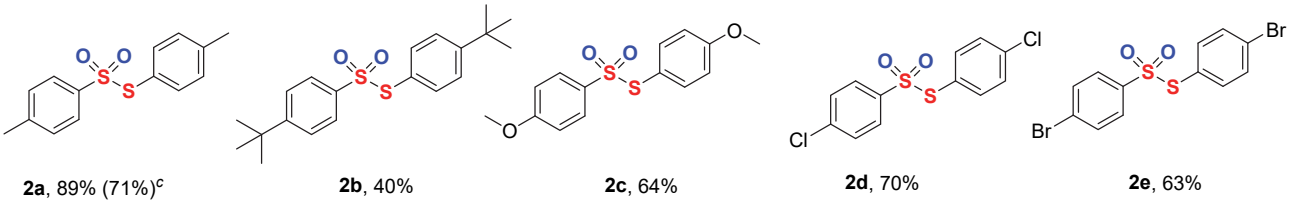
methane (DCM) (Table 1, Entries 9～12). After obtaining the optimal photo catalyst, oxidant and solvent, we tried to change the amounts of photocatalysts and oxidants. The results showed that the isolated yield of product **2** was decreased when decreasing catalyst and oxidation dose, but had no significant changes when increasing catalyst and oxidation dose (Table 1, Entries 15～18). After the establishment of reaction system for the selective aerobic oxidation of thiol, some additional screening experiments were subsequently performed. It was found that the product was not detected when reaction was conducted in the absence of catalyst, oxidant or blue LEDS (Table 1, Entries 13, 14 and 19), indicating that the light-irradiation and additive are indispensable condition for this reaction. Furthermore, there was no improvement in isolated yield when the reaction atmosphere and time were altered (Entries 20 and 21). The effect of different color light sources (blue, white and green) on the reaction was investigated. It can be seen that the maximum yield could be obtained using blue light source. Then, the effect of different powers (30, 18, 10 and 5 W) of blue light source was further studied. Under the same conditions, the yield of the reaction was decreased with the decrease of power. Although the reaction yield could be slightly increased from 89% to 91% when the light source power was changed from 18 W to 30 W. 18 W was used in the following experiment because of environmental reason. Overall, the optimized conditions were as follows: **1** (0.5 mmol), eosin Y (5.0 mol%), selectfluor (2.0 equiv.) under O_2 in CH_3CN/H_2O (V∶V=1∶1) at room temperature for 6 h.

With the optimal conditions in hand, the coupling reactions of various thiol were then examined (Table 2). As expected, the thiophenols with the electron-rich group such as methyl, tertiary butyl and methoxy groups could be converted into the desired products (**2a**～**2c**, **2g**) in 40%～89% yields. Among them, the yields of **2b** and **2g** were relatively low due to the steric hindrance of substituents. Moreover, the thiophenols bearing halogen groups on *ortho*-, *meta*- and *para*-positions could also undergo the reaction smoothly to give the target products (**2d**～**2f**, **2h**～**2m**) in moderate to good yields. However, the yields of the thiophenols containing bromo group were lower than those of thiophenols containing other halogen groups (F, Cl) (**2d**～**2f**). Other aromatic thiols, such as thiophenol, heterocycle as well as polycyclic arene were also suitable in this protocol to provide the corresponding thiosulfonates (**2n**～**2p**) in 46%～74% yields.

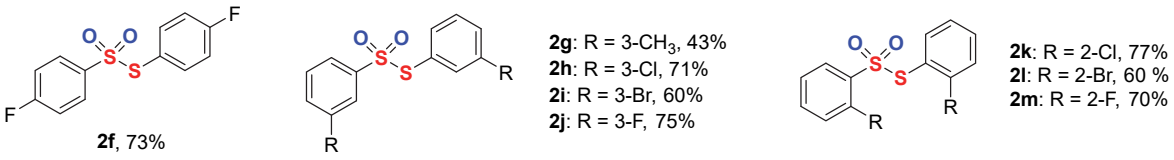
To further study the substrate scope of this protocol, our attention was then transfered to the synthesis of unsymmetrical thiosulfonates (Table 3). The unsymmetrical thiosulfonates **3a**～**3c** were obtained in moderate yields by the reaction of ethanethiol with different thiophenols. It should be noted that the linear aliphatic thiols such as butanethiol and heptanethiol were also suitable for this reaction, and the corresponding thiosulfonates (**3d**, **3i**, **3j**) were obtained in 30%～46% yields. Of note, the cyclohexanethiol could also react with various substituted thiols reactions to obtain the corresponding products (**3f**, **3g**). In addition, the case of unsymmetrical thiosulfonate (**3d**) was

Table 2 Substrate scope of symmetrica thiosulfonates[a,b]





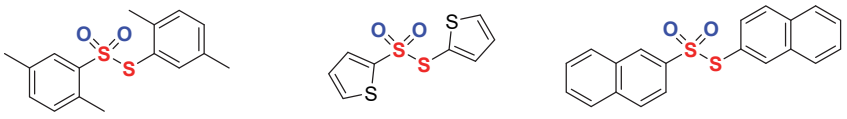
2a, 89% (71%)[c] **2b**, 40% **2c**, 64% **2d**, 70% **2e**, 63%



2f, 73%

2g: R = 3-CH_3, 43%
2h: R = 3-Cl, 71%
2i: R = 3-Br, 60%
2j: R = 3-F, 75%

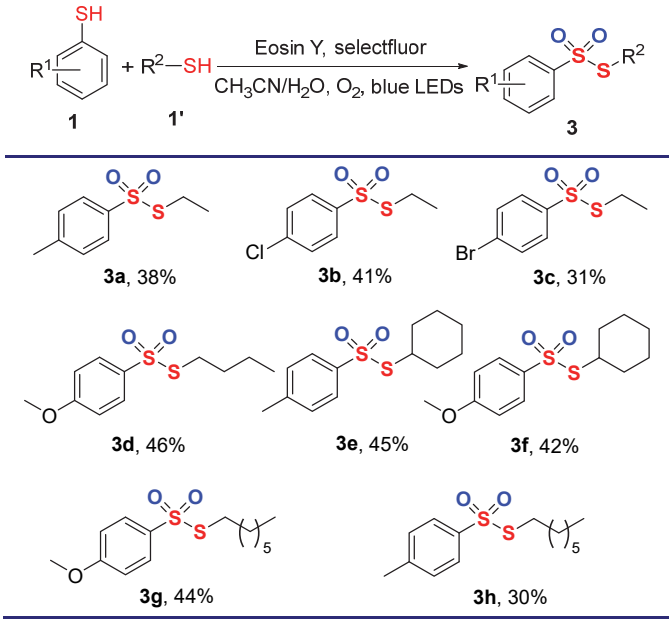
2k: R = 2-Cl, 77%
2l: R = 2-Br, 60 %
2m: R = 2-F, 70%



2n, 46% **2o**, 70% **2p**, 74%

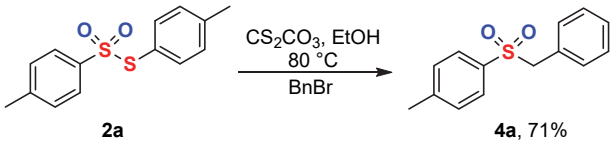
[a] Reaction conditions: **1** (0.5 mmol), Eosin Y (5.0 mol%), selectfluor (2.0 equiv.), CH_3CN/H_2O (3 mL, V∶V=1∶1), r.t., 6 h, O_2. [b] Isolated yields. [c] Gram-scale synthesis (**1a**, 5 mmol).

Table 3 Substrate scope of unsymmetrical thiosulfonates esters[a,b]



[a] Reaction conditions: **1** (0.25 mmol), **1'** (0.25 mmol), eosin Y (5.0 mol%), selectfluor (2.0 equiv.), CH_3CN/H_2O (3 mL, $V:V=1:1$), r.t., 6 h, O_2. [b] Isolated yields.

explored. The two intermolecular coupling products, alkyl thiosulfonate and aryl thiosulfonate, and the target product were obtained in the ratio of 2∶4∶4. Thus, this reaction provided a novel method for the selective synthesis of unsymmetrical thiosulfonates **3**. Furthermore, the prepared thiosulfonate (**2a**) could react with benzyl bromide to give unsymmetric sulfone (**4a**) in the presence of Cs_2CO_3 (Scheme 2). Successful implementation of the above-mentioned transformation clearly reveals that such protocol has a good synthetic utility.



Scheme 2 Practical application experiment

To figure out a plausible mechanism for this transformation, preliminary mechanism investigation was performed (Scheme 3). The ^{18}O-labeled experiments were carried out by using $^{18}O_2$ and $H_2{}^{18}O$ as the ^{18}O-reagents. The isotope of ^{18}O was found in the product in the presence of $H_2{}^{18}O$ rather than $^{18}O_2$. These results implied that the oxygen-atom of product came from H_2O.

Based on the above results and related literature[15-20], a plausible mechanism was proposed. Initially, thiophenol **1** is oxidized to thiol radical cation **A** by eosin Y, then thiol radical cation **A** is combined into disulfides **B**. Subsequently, one of the sulfur atoms of disulfides is fluorinated by selectfluor to form a sulfonium ion, and successive substitution of the fluorine atom by water provides a thiosulfinate **C**. The unchanged sulfur atom of thiosulfinate is further oxidized via a similar mechanism to produce an unstable disulfoxide **D**, which immediately rearranges to form a stable symmetrical **E** or unsymmetrical thiosulfonate **F** (Scheme 4).

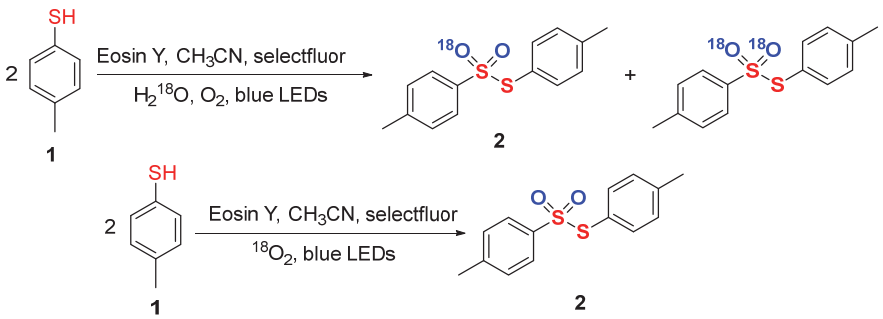
3 Conclusions

In conclusion, a photocatalytic protocol of various thiosulfonates in moderate-to-good yields from simple reactants under mild conditions was firstly reported. This method could prepare symmetric/asymmetric thiosulfonates by photocatalytic oxidative cross-coupling under relatively mild conditions with good functional group tolerance and high yield. Thus, this work provides a strategy for achieving an efficient and controllable conversion of sulfur-containing organics.

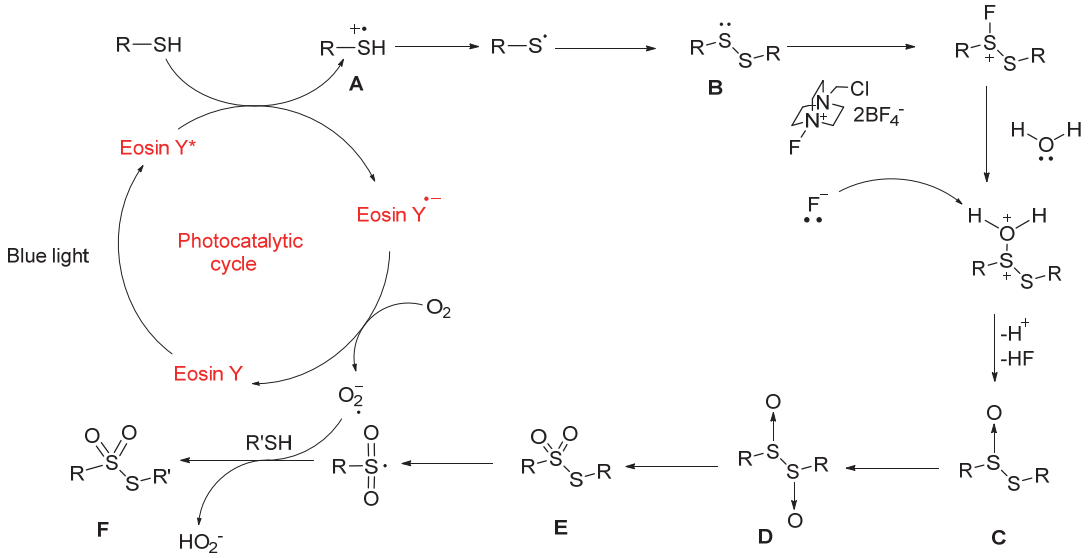
4 Experimental sections

4.1 General information

All the chemicals were obtained commercially and used without any prior purification. All products were isolated by short chromatography on a silica gel (200～300 mesh) column using petroleum ether (60～90 ℃) and ethyl acetate. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 500 spectrometer at ambient temperature with tetramethylsilane (TMS) as the internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer.



Scheme 3 Control experiments



Scheme 4 Plausible mechanism

4.2 General procedure for the synthesis of **2**

To a 15 mL Schlenk-tube were charged with **1** (0.5 mmol), eosin Y (0.025 mmol) and selectfluor (1.0 mmol). The mixture of CH_3CN/H_2O (3 mL, V∶V=1∶1) was injected in the tube. After the tube was evacuated and backfilled with O_2 for three times, the reaction was irradiated by 18 W blue LEDs for 6 h. The reaction was then quenched with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was further purified by silica gel column chromatography (200～300 mesh silica gel, petroleum ether/ethyl acetate, V∶V=10∶1) to afford product **2**.

S-(*p*-Tolyl)-4-methylbenzenesulfonothioate (**2a**): Yellow solid, 89% yield. m.p. 76～77 ℃ (lit.[11] 73.8～75.2 ℃); ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.45 (d, J=7.5 Hz, 2H), 7.39 (d, J=8.0 Hz, 2H), 7.25 (d, J=8.0 Hz, 2H), 7.21 (d, J=7.5 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 145.56, 142.61, 140.12, 136.51, 130.87, 130.33, 127.62, 124.21, 21.60, 21.41; HRMS (ESI-TOF) calcd for $C_{14}H_{14}O_2S_2Na$ [M+Na]$^+$ 301.0327, found 301.0329.

S-(4-(*tert*-Butyl)phenyl)-4-(*tert*-butyl)benzenesulfonothioate (**2b**): White solid, 40% yield. m.p. 150～151 ℃ (lit.[11] 149.5～151.4 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44～7.40 (m, 2H), 7.35～7.31 (m, 2H), 7.28～7.24 (m, 2H), 7.20 (dd, J=9.3, 2.8 Hz, 2H), 1.26 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.57, 155.05, 140.25, 136.34, 127.47, 126.47, 125.68, 124.66, 35.28, 34.95, 31.11; HRMS (ESI-TOF) calcd for $C_{20}H_{26}O_2S_2Na$ [M+Na]$^+$ 385.1266, found 385.1271.

S-(4-Methoxyphenyl)-4-methoxybenzenesulfonothioate (**2c**): Brown solid, 64% yield. m.p. 72～74 ℃ (lit.[11] 73.8～75.2 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46～7.39 (m, 2H), 7.23～7.16 (m, 2H), 6.83～6.78 (m, 2H), 6.79～6.75 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.54, 162.23, 138.38, 134.94, 129.92, 118.94, 114.93, 113.85, 55.72, 55.49; HRMS (ESI-TOF) calcd for $C_{14}H_{14}O_4S_2Na$ [M+Na]$^+$ 333.0226, found 333.0223.

S-(4-Chlorophenyl)-4-chlorobenzenesulfonothioate (**2d**): Yellow solid, 70% yield. m.p. 135～137 ℃ (lit.[11] 134.7～136.5 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54～7.50 (m, 2H), 7.46～7.41 (m, 2H), 7.39～7.33 (m, 2H), 7.33～7.30 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.27, 139.55, 137.55, 136.67, 128.91, 128.26, 127.92, 124.99.

S-(4-Bromophenyl)-4-bromobenzenesulfonothioate (**2e**): Brown solid, 63% yield. m.p. 144～146 ℃ (lit.[11] 63.7～65.5 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, J=8.6 Hz, 2H), 7.52 (d, J=8.4 Hz, 2H), 7.44 (d, J=8.6 Hz, 2H), 7.25 (t, J=6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.84, 136.82, 131.91, 131.27, 128.18, 127.93, 126.01, 125.58.

S-(4-Fluorophenyl)-4-fluorobenzenesulfonothioate (**2f**): White solid, 73% yield. m.p. 64～66 ℃ (lit.[11] 147.0～148.4 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.57～7.47 (m, 2H), 7.29 (dd, J=7.6, 5.9 Hz, 2H), 7.05 (t, J=8.4 Hz, 2H), 6.98 (t, J=8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 166.65, 165.91, 164.60, 163.88, 138.85, 130.47, 123.26, 117.06, 116.96, 116.33, 116.15.

S-(*m*-Tolyl)-3-methylbenzenesulfonothioate (**2g**):[21] Colorless oil, 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29 (dd, J=14.4, 7.1 Hz, 3H), 7.22 (dd, J=15.8, 8.0 Hz, 2H), 7.17～7.13 (m, 1H), 7.07 (dd, J=7.2, 0.5 Hz, 2H), 2.27 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 142.78, 139.42, 139.03, 137.21, 134.33, 133.64, 132.20, 129.15, 128.57, 128.03, 127.63, 124.75, 21.16, 21.14.

(3-Chlorophenyl)-3-chlorobenzenesulfonothioate (**2h**):[21] Colorless oil, 71% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.89～7.85 (m, 1H), 7.70 (ddd, J=6.8, 8.9, 4.4 Hz, 2H), 7.58 (d, J=8.0 Hz, 1H), 7.54～7.49 (m, 2H), 7.40～7.35 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 143.54, 135.94, 135.43, 135.11, 134.60, 134.33, 132.56, 132.06,

128.99, 127.19, 126.38.

S-(3-Bromophenyl)-3-bromobenzenesulfonothioate (**2i**): Colorless oil, 60% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.04～7.99 (m, 1H), 7.86～7.81 (m, 1H), 7.64～7.56 (m, 3H), 7.49～7.41 (m, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 143.62, 138.71, 137.99, 135.80, 135.41, 132.36, 132.34, 130.00, 129.21, 126.66, 122.73, 122.62; HRMS (ESI-TOF) calcd. for $C_{12}H_8Br_2O_2S_2Na$ $[M+Na]^+$ 428.8332, found 428.8336.

S-(3-Fluorophenyl)-3-fluorobenzenesulfonothioate (**2j**):[11] Colorless oil, 75% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.69～7.65 (m, 2H), 7.54～7.48 (m, 2H), 7.45～7.40 (m, 2H), 7.29～7.26 (m, 1H), 7.24～7.20 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 163.11, 161.13, 143.84, 132.97, 132.42, 132.13, 128.83, 124.08, 123.29, 122.51, 119.82, 114.82.

S-(2-Chlorophenyl)-2-chlorobenzenesulfonothioate (**2k**):[22] Colorless oil, 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (d, J=7.7 Hz, 1H), 7.55 (dt, J=13.7, 7.7 Hz, 3H), 7.38 (dt, J=15.0, 6.9 Hz, 2H), 7.31～7.23 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.40, 140.38, 139.98, 134.80, 133.16, 133.01, 132.49, 131.07, 130.30, 127.72, 126.78, 126.65.

S-(2-Bromophenyl)-2-bromobenzenesulfonothioate (**2l**):[22] Colorless oil, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (d, J=7.9 Hz, 1H), 7.63 (dd, J=7.7, 1.6 Hz, 1H), 7.51 (dd, J=8.0, 1.4 Hz, 1H), 7.47 (dd, J=7.9, 1.2 Hz, 1H), 7.36 (td, J=7.7, 1.5 Hz, 1H), 7.28 (td, J=7.5, 1.2 Hz, 1H), 7.25～7.19 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 143.62, 138.71, 137.99, 135.80, 135.41, 132.36, 132.24, 130.00, 129.21, 126.66, 122.73, 122.62.

S-(2-Fluorophenyl)-2-fluorobenzenesulfonothioate (**2m**): Colorless oil, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65～7.59 (m, 1H), 7.54～7.43 (m, 3H), 7.27～7.23 (m, 1H), 7.20～7.11 (m, 2H), 7.05 (t, J=8.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 162.92, 158.89, 139.08, 136.46, 134.58, 131.11, 130.22, 125.13, 123.92, 117.65, 116.35, 114.74; HRMS (ESI-TOF) calcd. for $C_{12}H_8F_2O_2S_2Na$ $[M+Na]^+$ 308.9826, found 308.9836

S-(2,5-Dimethylphenyl)-2,5-dimethylbenzenesulfonothioate (**2n**):[11] Colorless oil, 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27～7.24 (m, 1H), 7.20 (d, J=7.5 Hz, 2H), 7.11 (dd, J=17.7, 7.7 Hz, 2H), 6.92 (s, 1H), 2.61 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.04, 140.55, 138.71, 136.41, 135.74, 134.63, 134.35, 132.71, 132.50, 130.69, 130.60, 126.77, 20.53, 20.44, 20.09, 19.98.

S-(Thiophen-2-yl)-thiophene-2-sulfonothioate (**2o**): Yellow solid, 70% yield. m.p. 58～60 ℃ (lit.[11] 57.2～58.9 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (dd, J=5.0, 1.2 Hz, 1H), 7.67～7.62 (m, 1H), 7.41 (dd, J=3.8, 1.2 Hz, 1H), 7.25 (dd, J=3.7, 1.1 Hz, 1H), 7.11 (dd, J=5.3, 3.7 Hz, 1H), 7.06 (dd, J=4.9, 3.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 142.56, 139.63, 135.60, 134.56, 134.47, 128.52, 127.31, 125.19.

S-(Naphthalen-2-yl)naphthalene-2-sulfonothioate (**2p**): Yellow solid, 74% yield. m.p. 101～103 ℃ (lit.[11] 98.7～101.5 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (d, J=1.3 Hz, 1H), 7.88 (dd, J=8.5, 4.5 Hz, 2H), 7.84～7.80 (m, 2H), 7.72 (d, J=8.5 Hz, 1H), 7.68～7.63 (m, 3H), 7.61 (d, J=8.4 Hz, 1H), 7.58～7.50 (m, 2H), 7.49～7.44 (m, 1H), 7.34 (dd, J=8.5, 1.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.68, 137.72, 135.14, 134.13, 133.28, 131.86, 131.63, 129.48, 129.42, 129.35, 129.15, 128.42, 128.27, 127.91, 127.75, 127.70, 126.93, 125.19, 122.44.

4.3 General procedure for the synthesis of **3**

To a 15 mL Schlenk-tube were charged with **1** (0.25 mmol), **1'** (0.25 mmol), eosin Y (0.025 mmol) and selectfluor (1.0 mmol). The mixture of CH_3CN/H_2O (3 mL, V∶V=1∶1) was injected in the tube. After the tube was evacuated and backfilled with O_2 for three times, the reaction was irradiated by 18 W blue LEDs for 6 h. The reaction was then quenched with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was further purified by silica gel column chromatography (200～300 mesh silica gel, petroleum ether/ethyl acetate, V∶V=10∶1) to afford product **3**.

S-Ethyl-4-methylbenzenesulfonothioate (**3a**): Yellow solid, 38% yield. m.p. 95～98 ℃ (lit.[11] 96.8～98.4 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, J=8.1 Hz, 2H), 7.29～7.24 (m, 2H), 3.22～3.14 (m, 2H), 2.40 (s, 3H), 1.45 (t, J=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 142.27, 136.17, 130.63, 124.45, 53.54, 21.48, 8.35.

S-Ethyl-4-chlorobenzenesulfonothioate (**3b**): Colorless oil, 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, J=8.5 Hz, 2H), 7.37 (d, J=8.5 Hz, 2H), 3.14 (d, J=7.4 Hz, 2H), 1.39 (t, J=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.36, 137.34, 130.13, 126.32, 54.20, 8.37; HRMS (ESI-TOF) calcd. for $C_8H_9ClO_2S_2Na$ $[M+Na]^+$ 258.9625, found 258.9619.

S-Ethyl-4-bromobenzenesulfonothioate (**3c**): Colorless oil, 31% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62～7.58 (m, 2H), 7.57～7.52 (m, 2H), 3.21 (q, J=7.4 Hz, 2H), 1.45 (dd, J=8.8, 6.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.50, 133.11, 126.93, 126.75, 54.24, 8.38; HRMS (ESI-TOF) calcd. for $C_8H_9BrO_2S_2Na$ $[M+Na]^+$ 302.9120, found 302.9131.

S-Butyl-4-methoxybenzenesulfonothioate (**3d**):[23] Colorless oil, 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (d, J=8.8 Hz, 2H), 6.86 (d, J=8.8 Hz, 2H), 3.80 (s, 3H), 2.77～2.69 (m, 2H), 1.65 (dt, J=14.9, 7.4 Hz, 2H), 1.38 (dd, J=14.9, 7.4 Hz, 2H), 0.88 (t, J=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 159.49, 131.64, 128.56, 114.63, 55.41, 38.54, 30.80, 21.64, 13.66.

S-Cyclohexyl-4-methylbenzenesulfonothioate (**3e**):[24] Colorless oil, 45% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, J=6.2 Hz, 2H), 7.11 (d, J=6.7 Hz, 2H), 2.79 (ddd, J=10.6, 7.0, 2.4 Hz, 1H), 2.32 (s, 3H), 2.01 (d, J=12.0 Hz, 2H), 1.75 (d, J=9.1 Hz, 2H), 1.59 (s, 2H), 1.35～1.22 (m, 4H; ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.50, 135.02, 129.62, 127.59, 49.77, 32.62, 26.03, 25.62, 21.02; HRMS (ESI-TOF-MS) calcd. for $C_{13}H_{18}O_2S_2Na$ $[M+Na]^+$

293.0641, found 293.0645.

S-Cyclohexyl-4-methoxybenzenesulfonothioate (**3f**):[23] Colorless oil, 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52～7.43 (m, 2H), 6.91～6.81 (m, 2H), 3.79 (s, 3H), 2.79 (tt, J=10.7, 3.7 Hz, 1H), 2.01 (d, J=10.2 Hz, 2H), 1.80～1.69 (m, 2H), 1.64～1.53 (m, 1H), 1.41～1.14 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 159.16, 130.73, 129.38, 114.55, 55.40, 49.69, 32.60, 26.03, 25.67.

S-Heptyl-4-methoxybenzenesulfonothioate (**3g**): Colorless oil, 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 3.80 (s, 3H), 2.72 (t, J=7.3 Hz, 2H), 1.68～1.64 (m, 2H), 1.28 (ddd, J=15.2, 10.8, 5.1 Hz, 8H), 0.87 (t, J=6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 159.49, 131.65, 128.60, 114.62, 55.40, 38.92, 31.70, 28.86, 28.73, 28.45, 22.61, 14.09; HRMS (ESI-TOF) calcd. for $C_{14}H_{22}O_3S_2Na$ $[M+Na]^+$ 325.0903, found 325.0909.

S-Heptyl-4-methylbenzenesulfonothioate (**3h**): Colorless oil, 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 (d, J=8.2 Hz, 2H), 7.13 (d, J=8.0 Hz, 2H), 2.75～2.70 (m, 2H), 2.33 (s, 3H), 1.68～1.64 (m, 2H), 1.30～1.22 (m, 8H), 0.87 (t, J=7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.96, 134.25, 129.71, 128.38, 38.97, 31.69, 28.85, 28.77, 28.44, 22.60, 21.04, 14.08; HRMS (ESI-TOF-MS) calcd. for $C_{14}H_{22}O_2S_2$ $[M+Na]^+$ 309.0953, found 309.0961.

4.4 Synthesis of **4a**

Benzyl bromide (0.50 mmol) was added to a mixture of *S*-(*p*-tolyl)-4-methylbenzenesulfonothioate (0.25 mmol) and Cs_2CO_3 (0.125 mmol) in a sealed tube. After 0.5 mL of EtOH was added to the reaction, the vessel was closed and the mixture stirred at 80 ℃ for 16 h to afford 1-(benzylsulfonyl)-4-methylbenzene (**4a**), Colorless oil, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50 (d, J=8.2 Hz, 2H), 7.31 (t, J=7.3 Hz, 1H), 7.26 (t, J=7.1 Hz, 2H), 7.23 (d, J=8.3 Hz, 2H), 7.09 (d, J=7.3 Hz, 2H), 4.29 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 135.00 (s), 130.84 (s), 129.52 (s), 128.79～128.46 (m), 128.32 (s), 62.94 (s), 21.65 (s); HRMS (ESI-TOF-MS) calcd. for $C_{14}H_{14}O_2SNa$ $[M+Na]^+$ 269.0608, found 269.606.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **2a**～**2h**, **2a**～**2h** and **4a**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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