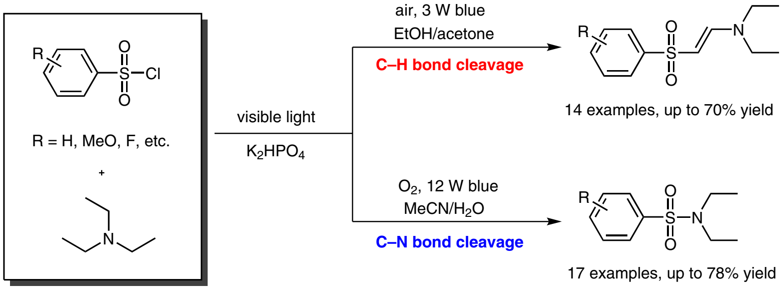
Eosin Y-Sensitized Photocatalytic Reaction of Tertiary Aliphatic Amines with Arenesulfonyl Chlorides under Visible-Light Irradiation

Yuguo Cai[a,b]
Ronghua Zhang*[a,b]
Deli Sun[a,b]
Song Xu[a,b]
Qiguang Zhou[a,b]

[a] School of Chemistry Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. of China
[b] Shanghai Key Lab of Chemical Assessment and Sustainability, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. of China
rhzhang@tongji.edu.cn



Received: 08.03.2017
Accepted after revision: 18.04.2017
Published online: 10.05.2017
DOI: 10.1055/s-0036-1588828; Art ID: st-2017-w0167-l

Abstract A mild, practical, and environmentally friendly route to vinyl sulfones and sulfonamides has been developed based on the reaction of aliphatic amines with arenesulfonyl chlorides in the presence of eosin Y as a photocatalyst under visible light. The method permits the selective formation of vinyl sulfones or sulfonamides, depending on the oxidation environment and solvent. A wide range of products were obtained in moderate to good yields under the optimized conditions.

Key words vinyl sulfones, sulfonamides, eosin Y, photoredox catalysis, amines, arenesulfonyl chlorides

Chemists constantly seek more efficient and more economical methods for synthesis. Sunlight is a ubiquitous natural resource that is easy to obtain and is nonpolluting.[1,2] However, most of the light from the sun is visible light, and most organic molecules do not absorb light in the visible region.[3] Consequently, a photosensitizer is generally required to induce visible-light-driven organic reactions.[4–8] In recent years, the groups of Yoon,[6,9–11] Stephenson,[12,15] MacMillan,[16–19] among others,[20–28] have demonstrated that visible-light photosensitizers can be applied in new methods of promoting chemical transformations.[29]

The photosensitizers can be roughly divided into three categories: transition-metal photosensitizers such as ruthenium or iridium complexes,[30–33] semiconductor photosensitizers such as dye-sensitized TiO$_2$ or metal-sensitized TiO$_2$,[34,35] and organic dyes such as eosin Y, rose bengal, or methylene blue.[3,36–38] Some of the transition-metal complexes are expensive, potentially toxic, and not sustainable. Organic dyes have shown advantages in some organic reactions in that they are easy to handle, inexpensive, and environmentally friendly. In particular, eosin Y has been widely used as a photosensitizer in synthetic chemistry.[38–40]

The synthesis of vinyl sulfones and sulfonamides has aroused great interest because of their biological activities, for example as diuretic agents, antithyroid agents, or hypoglycemics.[41–43] Vinyl sulfones are important intermediates and reagents for the synthesis of organic compounds,[44–47] some of which have been reported to be powerful inhibitors of enzymes such as cysteine proteases[48,49] or sortase.[50,51] Sulfonamides are widely used as intermediates in the manufacture of agrochemicals and clinical drugs.[52,53] Taking into account the importance of vinyl sulfones and sulfonamides, we need to develop more synthetic methods to satisfy the need for such compounds. In addition, compared with tertiary aromatic amines, little attention has been paid to simple tertiary aliphatic amines.

In 2012, Stephenson and co-workers reported that tosyl chloride produces a sulfonyl radical on irradiation by visible light.[54] In 2013, Yu and co-workers reported the synthesis of β-amidovinyl sulfones from enamides and sulfonyl chlorides through visible-light photoredox catalysis.[29] In 2014, Zheng and co-workers performed the same reaction with $[Ru(bpy)_3]^{2+}$ as a photoredox catalyst.[55] In 2016, Yuan and co-workers reported that the reaction of triethylamine with sodium 4-methylbenzenesulfinate affords sulfonamides and β-arenesulfonyl enamines.[56] On the basis of these works, we investigated the aerobic oxidative reaction of tertiary aliphatic amines with arenesulfonyl chlorides to form the corresponding vinyl sulfones and sulfonamides in the presence of eosin Y as a photosensitizer, as an environmentally friendly method that avoids the use of transition-metal catalysts.

We began by studying the reaction of tosyl chloride (**1a**, 0.2 mmol) with triethylamine (**2a**, 1 mmol) in MeCN (6 mL) in the presence of 3 mol% eosin Y as a photocatalyst with irradiation by a 3 W blue light-emitting diode (LED) under air. After 60 minutes, the configurationally pure (*E*)-*N*,*N*-diethyl-2-(4-toluenesulfonyl)ethylenamine (**3a**) and *N*,*N*-diethyl-4-toluenesulfonamide (**4a**) were isolated in 45 and 15% yield, respectively (Table 1, entry 1). We then carried out a number of control experiments. Under an O_2 atmosphere, we obtained **4a** and **3a** in 50 and 10% yield, respectively (entry 2). The use of N_2 instead of air gave **3a** exclusively in 20% yield, with no **4a** (entry 3). In the absence of eosin Y, the reaction did not proceed, as indicated by TLC (entry 4). Solvent optimization showed that 1:2 EtOH–acetone was the best solvent for the formation of **3a** (entries 5–7). We then examined the effects of additives (entries 8–17). When we screened various organic dyes as photocatalysts, we found that eosin Y gave higher yields than did methylene blue, rose bengal, or fluorescein (entries 8–11). By examining various LEDs, we found that the 3 W blue LEDs gave higher yields of the vinyl sulfone. We then screened oxidation environments, solvents, and LEDs to identify better conditions for obtaining sulfonamides (entries 14–17). These experimental results clearly indicated that the oxidation environment had a remarkable effect on the selectivity toward products **3a** and **4a** (entries 1–3, 8, and 14). Furthermore, an appropriate choice of solvent, LED, and temperature can improve the yields of **4a** (entries 17–19).

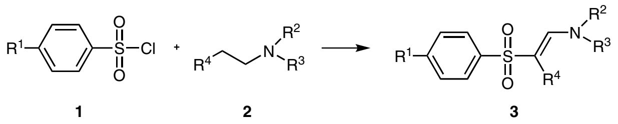
We next investigated the reaction of various arenesulfonyl chlorides **1** with tertiary aliphatic amines **2** to give vinyl sulfones **3** under an air oxidation environment with 3 W blue LED irradiation and 1:2 EtOH–acetone as solvent. As shown in Table 2, electron-neutral arenesulfonyl chlorides **1** reacted with tertiary amines **2** to give the corresponding products **3a**,**b**,**d** in moderate to good yields. Electron-deficient arenesulfonyl chlorides also participated in this transformation to give a variety of vinyl sulfones **3e**–**i**. The reactions with 4-fluorobenzenesulfonyl chloride gave lower yields than those from 4-bromobenzenesulfonyl chloride or 4-chlorobenzenesulfonyl chloride (**3e**–**g**). An electron-rich arenesulfonyl chloride gave a slightly lower yield (**3c**). The reaction of arenesulfonyl chlorides with *N*,*N*-diisopropylethylamine (DIPEA) occurred at the terminal of the ethyl group rather than the isopropyl group (**3j** and **3k**). When tributylamine was used, we obtained the product (1*E*)-*N*,*N*-dibutyl-2-(4-tosyl)but-1-en-1-amine (**3l**). Moreover, cyclic amines also gave the expected products **3m** and **3n**.

Table 1 Optimization of Reaction Conditions[a]

Entry	Organic dye	Oxidant	Solvent	Additive	LED	Yield[b] of **3a**/**4a** (%)
1	eosin Y	air	MeCN	–	3 W blue	45/15
2	eosin Y	O_2[c]	MeCN	–	3 W blue	10/50
3	eosin Y	N_2[d]	MeCN	–	3 W blue	20/trace
4	none	air	MeCN	–	3 W blue	none
5	eosin Y	air	EtOH	–	3 W blue	50/10
6	eosin Y	air	acetone	–	3 W blue	45/13
7	eosin Y	air	EtOH–acetone (1:2)	–	3 W blue	60/trace
8	eosin Y	air	EtOH–acetone (1:2)	K_2HPO_4	3 W blue	67/trace
9	rose bengal	air	EtOH–acetone (1:2)	K_2HPO_4	3 W blue	35/trace
10	methylene blue	air	EtOH–acetone (1:2)	K_2HPO_4	3 W blue	30/trace
11	fluorescein	air	EtOH–acetone (1:2)	K_2HPO_4	3W blue	42/trace
12	eosin Y	air	EtOH–acetone (1:2)	K_2HPO_4	12 W blue	53/trace
13	eosin Y	air	EtOH–acetone (1:2)	K_2HPO_4	12 W green	45/trace
14	eosin Y	O_2[c]	EtOH–acetone (1:2)	K_2HPO_4	3 W blue	12/55
15	eosin Y	O_2[c]	EtOH–acetone (1:2)	K_2HPO_4	12 W blue	8/60
16	eosin Y	O_2[c]	EtOH–acetone (1:2)	K_2HPO_4	12 W green	10/55
17	eosin Y	O_2[c]	MeCN–H_2O(1:1)	K_2HPO_4	12 W blue	trace/75
18[e]	eosin Y	air	MeCN–H_2O(1:1)	K_2HPO_4	3 W blue	20/30
19[f]	eosin Y	air	MeCN–H_2O(1:1)	K_2HPO_4	3 W blue	8/54

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1 mmol), organic dye (3 mol%), solvent (6 mL), LED irradiation, under air, –5 to 5 °C for **3a** or r.t. for **4a**.
[b] Isolated yield of the product **3a** and **4a**.
[c] Under O_2 (1 atm, balloon).
[d] Under N_2.
[e] At –5 to 5 °C.
[f] At r.t.

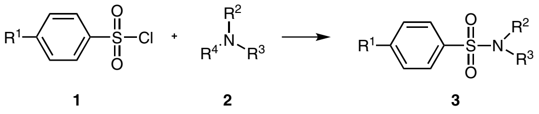
Table 2 Synthesis of Vinyl Sulfones **3**[a]



Product	R^1	R^2	R^3	R^4	Yield (%)[b]
3a	Me	Et	Et	H	67
3b	H	Et	Et	H	65
3c	OMe	Et	Et	H	63
3d	*t*-Bu	Et	Et	H	70
3e	F	Et	Et	H	54
3f	Cl	Et	Et	H	58
3g	Br	Et	Et	H	56
3h	NO_2	Et	Et	H	50
3i	CF_3	Et	Et	H	52
3j	Me	*i*-Pr	*i*-Pr	H	62
3k	H	*i*-Pr	*i*-Pr	H	63
3l	Me	*n*-Bu	*n*-Bu	Et	68
3m	Me	Et	$–CH_2CH_2CH_2–$		54
3n	H	Et	$–CH_2CH_2CH_2–$		56

[a] Reaction conditions: **1** (0.2 mmol), **2** (1 mmol), eosin Y (3 mol%), 1:2 EtOH–acetone (6 mL), K_2HPO_4 (1.5 equiv), 3 W blue LED, air, –5 to 5 for **3a**.
[b] Isolated yield.

Table 3 Synthesis of Sulfonamides **4**[a]



Product	R^1	R^2	R^3	R^4	Yield (%)[b]
4a	Me	Et	Et	Et	75
4b	H	Et	Et	Et	70
4c	OMe	Et	Et	Et	75
4d	*t*-Bu	Et	Et	Et	78
4e	F	Et	Et	Et	68
4f	Cl	Et	Et	Et	70
4g	Br	Et	Et	Et	68
4h	NO_2	Et	Et	Et	65
4i	AcHN	Et	Et	Et	63
4j	Me	*n*-Pr	*n*-Pr	*n*-Pr	72
4k	Cl	*n*-Pr	*n*-Pr	*n*-Pr	68
4l	H	*n*-Pr	*n*-Pr	*n*-Pr	65
4m	Me	*n*-Bu	*n*-Bu	*n*-Bu	75
4n	H	*n*-Bu	*n*-Bu	*n*-Bu	72
4o	Cl	*n*-Bu	*n*-Bu	*n*-Bu	70
4p	Me	$–(CH_2)_2O(CH_2)_2–$		Et	65
4q1 **4q2**	Me	Et	Et Me	Me Et	72 (**4q1**/**4q2** 1:2)

[a] Reaction conditions: **1** (0.2 mmol), **2** (1 mmol), eosin Y (3 mol%), MeCN–H_2O (6 mL), K_2HPO_4 (1.5 eq), 12 W blue LED, O_2 atmosphere, r.t.
[b] Isolated yield.

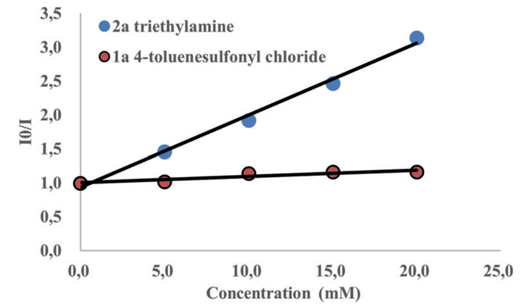
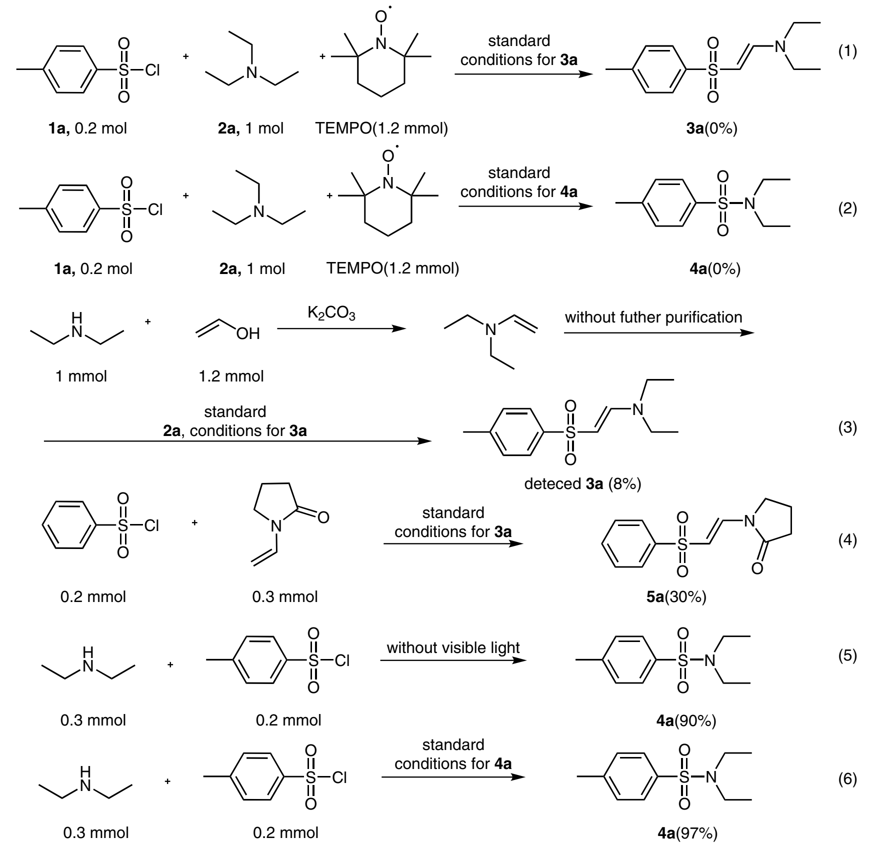


Figure 1 Emission quenching experiments with eosin Y

Next, we examined the reaction of trialkylamines **2** with various arenesulfonyl chlorides **1** for the synthesis of sulfonamides **4** (Table 3). We found that sulfonyl chlorides **1** with electron-withdrawing groups, such as F, Cl, Br, or nitro, or with electron-donating groups, such as methyl, *tert*-butyl, or methoxy, reacted well with triethylamine (**2a**) to give the corresponding sulfonamides **4a–i** in yields of 63–78%. In addition, various tertiary amines **2** were investigated under the optimized conditions. We found that symmetrical tertiary amines such as tripropylamine or tributylamine also gave the expected products **4i–o** in moderate to good yields. Next, we examined the reactions of asymmetric tertiary amines. *N*-Ethylmorpholine and diethyl(methyl)amine gave the corresponding products in acceptable yields; however, for the reaction of diethyl(methyl)amine, we obtained a 1:2 mixture of products **4q1** and **4q2**, possibly through of cleavage of the C–N bond.

We next carried out control experiments to elucidate the mechanism of the reaction. When the radical-trapping agent TEMPO (1.5 equiv) was added to reaction mixtures of **1a** and **2a** under the relevant standard conditions for the formation of **3a** or **4a**, we did not obtain either product (Scheme 1, eq. 1 and 2). Therefore, a sulfonyl radical might be an important radical intermediate. To determine whether the excited eosin Y was trapped by triethylamine, we performed fluorescence-quenching experiments. Stern–Volmer studies showed that triethylamine (**2a**) efficiently quenches the emissions from eosin Y (Figure 1).

We reasoned that an enamine might be an intermediate product. To test this hypothesis, we synthesized *N*,*N*-diethylethenamine by the reaction of acetaldehyde with diethylamine, with K_2CO_3 as the dehydrating agent. We then treated the enamine with **1a** without further purification, and we obtained **3a** (Scheme 1, eq. 3). In a further study, we



Scheme 1 Control experiments

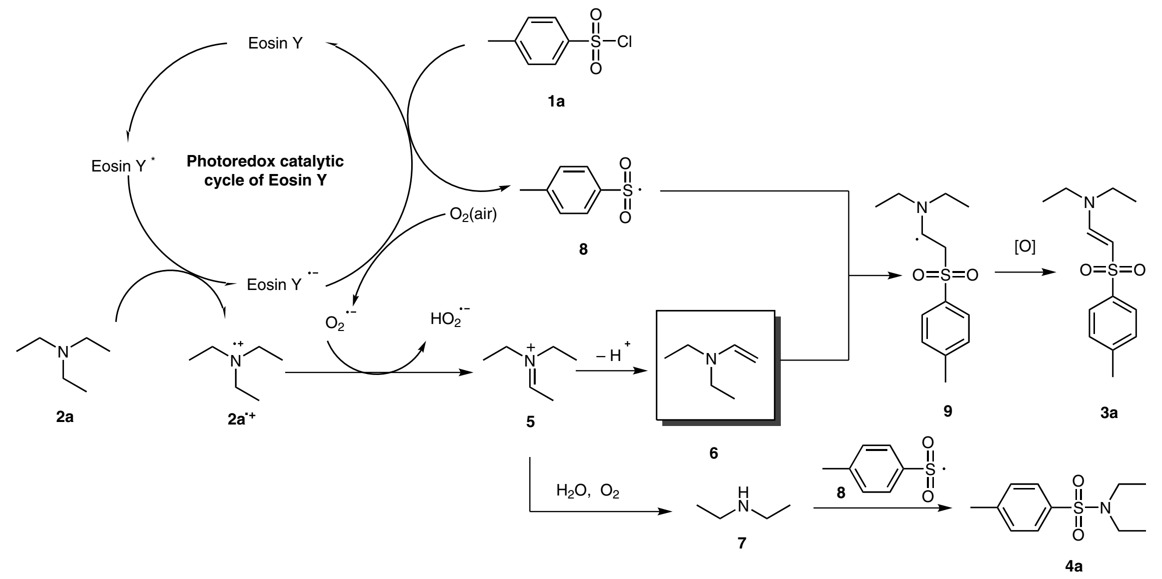
treated *N*-vinylpyrrolidone with **1a** under the standard conditions for formation of **3a** and we obtained the desired product **5a** (Scheme 1, eq. 4). Diethylamine and **1a** smoothly gave sulfonamide **4a** in 97% and 90% yield in the presence and absence of visible light, respectively (Scheme 1, eq. 6 and 5), proving that visible light promotes the formation of product **4a**.

On the basis of the above results and reports in the literature,[57,58] we propose the mechanism for the formation of vinyl sulfones and sulfonamides from tertiary aliphatic amines and arenesulfonyl chlorides that is shown in Scheme 2. The reaction begins with the photoexcitation of eosin Y (EY) catalyst by visible light to generate the excited state EY^*, which can undergo an oxidative or reductive quenching cycle.[59,60] In the reaction, EY^* is trapped by triethylamine (**2a**) and undergoes a reductive quenching cycle to form $EY^{\bullet -}$ and an amine radical cation $\mathbf{2a}^{\bullet +}$. By transferring a single electron to O_2 or **1a**, $EY^{\bullet -}$ regenerates EY, and **1a** reacts with O_2 to afford radical **8** and $O_2^{\bullet -}$. The latter then abstracts a hydrogen atom from $\mathbf{2a}^{\bullet +}$ to form $HO_2^{\bullet -}$ and iminium ion **5**, which can be transformed into enamine **6**.[56,58,59] Because intermediate **5** is unstable, it is easily hydrolyzed to give a secondary amine **7** in O_2 and water. Sulfonyl radical **8** then reacts with enamine **6** to provide the intermediate **9**. Radical **9** is oxidized and deprotonated to provide the desired vinyl sulfone **3a**, whereas the sulfonyl radical **8** attacks secondary amine **7** to afford target product **4a**.

In summary, we have described an efficient transition-metal-free method to synthesize vinyl sulfones[61] and sulfonamides[62] in good to moderate yields from arenesulfonyl chlorides and tertiary aliphatic amines by using eosin Y as a catalyst with irradiation by visible light. This method provides a mild, practical, and environmentally friendly procedure to synthesize vinyl sulfones or sulfonamides. The reaction is induced by visible-light irradiation with an organic dye as the photosensitizer and molecular oxygen as the terminal oxidant, without transition-metal ions or deleterious oxidants.

Funding Information

Natural Science Foundation of China 20972113/B020502



Scheme 2 Possible mechanism

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588828.

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(61) **(*E*)-*N*,*N*-Diethyl-2-(4-toluenesulfonyl)ethylenamine (3a); Typical Procedure**
A 10 mL round-bottomed flask equipped with magnetic stirring bar was charged with TsCl (**1a**; 0.2 mmol), Et$_3$N (**2a**; 1 mmol), eosin Y (3 mol%), K$_2$HPO$_4$ (1.5 equiv), and 1:2 EtOH–acetone (6 mL). The solution was then irradiated with 3 W blue LEDs at –5 to 5 °C under air. When the reaction was complete (TLC), the solvent was removed under reduced pressure and the crude product was purified by column chromatography [silica gel, PE–EtOAc (5:1)] to give a brown oil; yield: 31.48 mg (67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.75 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 12.7 Hz, 1 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 4.91 (d, *J* = 12.7 Hz, 1 H), 3.18 (br d, 4 H), 2.41 (s, 3 H), 1.17 (s, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 148.5, 142.3, 141.8, 128.5, 125.9, 91.4, 49.8, 42.4, 21.2, 14.5 11.0. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for C$_{13}$H$_{19}$NNaO$_2$S$^+$: 276.1020; found: 276.1029.

(62) ***N*,*N*-Diethyl-4-toluenesulfonamide (4a); Typical Procedure**
A 10 mL round-bottomed flask equipped with magnetic stirring bar was charged with TsCl (**1a**; 0.2 mmol), Et$_3$N (**2a**; 1 mmol), eosin Y (3 mol%), K$_2$HPO$_4$ (1.5 equiv), and 1:1 MeCN–H$_2$O (6 mL). The solution was then irradiated with 12 W blue LEDs at r.t. under an O$_2$ atmosphere. When the reaction was complete (TLC), the solvent was removed under reduced pressure and the crude product was purified by column chromatography [silica gel, PE–EtOAc (5:1)] to give a white solid; yield: 34.06 mg (75%); mp 60–62 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.70 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 3.23 (q, *J* = 7.2 Hz, 4 H), 2.43 (s, 3 H), 1.13 (t, *J* = 7.1 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.8, 137.2, 129.4, 126.9, 41.9, 21.3, 14.0. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for C$_{11}$H$_{17}$NNaO$_2$S$^+$: 250.0872; found: 250.0898.