Synthesis Y. Jian et al. Paper

Nitroacenaphthene as a New Photocatalyst for the Synthesis of Sulfonyl Amidines

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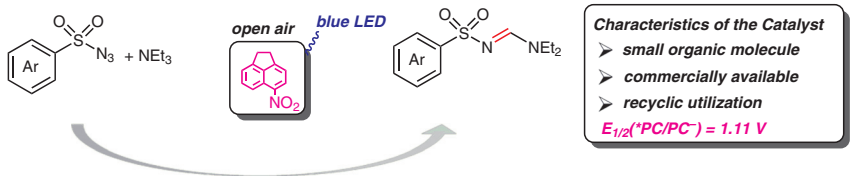

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Abstract A small molecule, namely nitroacenaphthene, is reported for the first time as a recyclable visible-light photocatalyst for the construction of the C=N bond from sulfonyl azides and amines. This scalable, site-selective protocol provides a convenient way to access various sulfonyl amidines under mild conditions. Two reaction pathways are proposed, according to different transformation patterns.

Key words nitroacenaphthene, photocatalyst, carbon-nitrogen double bond, sulfonyl amidines, *N*′-sulfonylimidamides, site selectivity

Photocatalytic synthesis is one of the most active fields in the organic chemistry community, and the relevant methodology has developed rapidly over the past decade.[1] The exploration of new photocatalytic reactivity of existing materials plays an essential role in the development of visible-light-mediated organic synthesis. The most commonly used photocatalysts are polypyridyl complexes based on transition metals (Ru, Ir)[2] and the newly reported Pt,[3] Cu,[4] Au,[5] and other metal[6] complexes, which provided an attractive platform for numerous novel, green synthetic strategies. However, the preparation of these photocatalysts generally requires high-cost starting materials, high temperatures, and multistep synthesis.[7] Meanwhile, available conjugated organic molecules have been found to display good visible-light-absorption ability and they have been used as elegant alternatives to metal complexes (Scheme 1A).[8] The past decade has witness their huge achievements in photocatalytic transformations.[9] For example, in 2014, Scaiano and co-workers disclosed α-sexithiophene was able to catalyze the dehalogenation of dibromo compounds under irradiation by visible light (Scheme 1B).[9a] In 2016, 4CzIPN was reported by Zhang and Luo as a perfect substitution for iridium complexes in the photoredox/nickel dual-catalytic system for decarboxylative cross-coupling (Scheme 1B).[9b] In 2019, Wang and co-workers realized decarboxylative arylation by using 3-amino-1-[4-(9*H*-carbazol-9-yl)phenyl]-9*H*-fluorene-2,4-dicarbonitrile (AFDC) as a photocatalyst under irradiation by 380–395 nm LEDs (Scheme 1B).[9e] Notably, Jiang and co-workers realized the construction of a chiral center with the catalytic system of dicyanopyrazine-derived chromophore (DPZ) and an asymmetric catalyst under visible-light irradiation (Scheme 1B).[10] In addition, high photocatalytic efficiency has been achieved by using different types of materials as carriers for the reported organic photocatalysts.[11] Despite of this great progress, the exploitation for more economical catalytic mode of non-metal substances still remains appealing. Herein we report a visible-light-induced synthesis of sulfonyl amidines through the application of nitroacenaphthene as a new photocatalyst, which is commercially available and exhibits excellent catalytic activity, chemical stability, and recyclability (Scheme 1C). During the preparation of this manuscript, a similar work was reported by Zeng and co-workers on the reaction of sulfonyl azides and amines using eosin Y as catalyst, but their substrates were limited to only arylsulfonyl azides and tertiary amines.[12]

Sulfonyl amidines are a fundamental class of building blocks in pharmaceutical molecules (Figure 1). Thus the syntheses of such compounds have attracted considerable interest from the realm of organic chemistry.[13] During our continuous investigations on the development of new photocatalytic reactions,[14] we found that sulfonyl amidine **3a** could be formed from sulfonyl azide **1a** and triethylamine (**2a**) with $Ru(bpy)_3Cl_2$ as a catalyst under visible light (Table 1, entry 1). Generally, most non-metal photocatalysts are organic dyes, which have also been used as fluorescent probes in chemical biology,[15] among which naphthalimide derivatives have been well-studied as representative examples.[16] We were intrigued to investigate of the application of such compounds as new photocatalysts in the preparation of **3a** instead of $Ru(bpy)_3Cl_2$.

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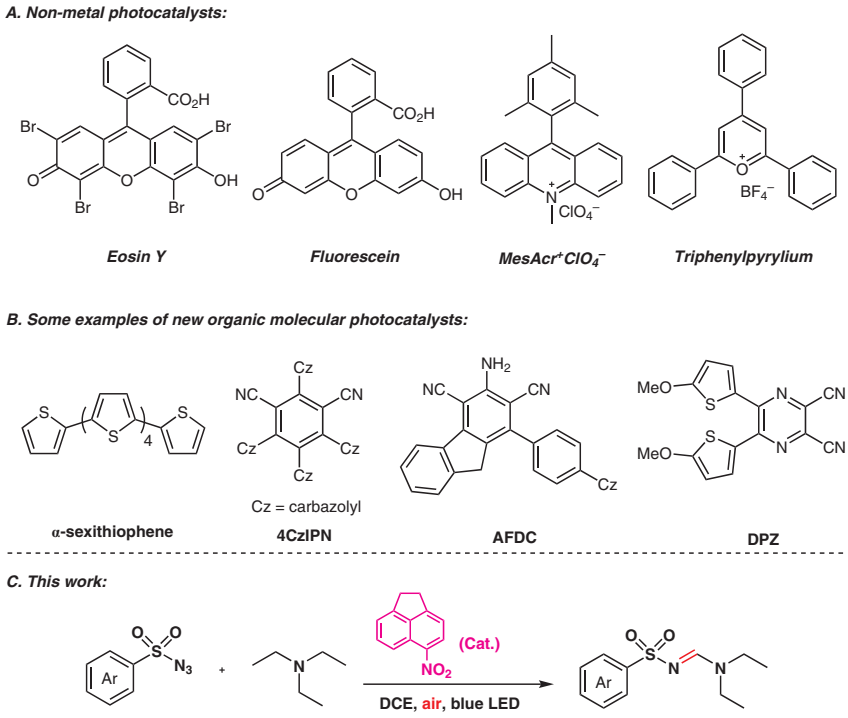


Scheme 1 Representative photocatalysts and this work

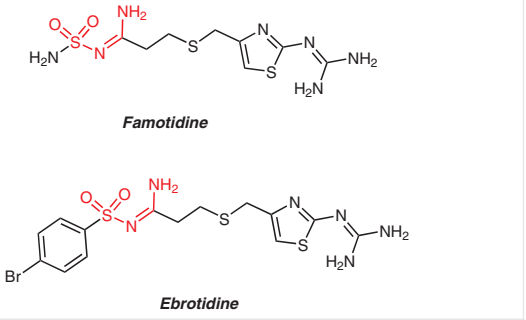
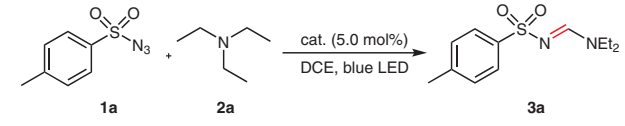


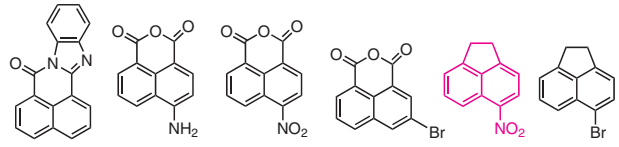
Figure 1 Selected post-marketing drugs containing the sulfonyl amidine structure

To confirm our hypothesis, a range of naphthalimide derivatives and their analogues were employed to run this protocol. To our delight, all of them were able to promote this transformation (Table 1, entries 2–7), among which nitroacenaphthene **cat. 5** was observed to give a higher yield than $Ru(bpy)_3Cl_2$ (66% vs 59%, entry 6). For comparison, the commonly used organic photocatalysts were also screened and these gave inferior results (entries 8–12). Control experiments revealed that both photocatalyst and blue LED were essential for the transformation, and air (O_2) might play an important role in catalytic cycles. (For more details of the conditions screening, see the Supporting Information.)

With the optimal conditions in hand, we firstly investigated the scope of sulfonyl azides. As listed in Scheme 2, sulfonyl azides with different substituent groups on the *para*-position of the benzene ring smoothly afforded the desired sulfonyl amidines **3a–g** in moderate to good yields (42–81%). Notably, strong electron-withdrawing groups, such as NO_2 or CF_3, were well tolerated with the standard conditions but with a negative effect on yields (**3f** and **3g**, 46% and 42% yields). Similarly, *ortho*- and *meta*-substituted sulfonyl azides afforded the desired amidines **3h–n** as well under the optimized conditions. Besides, substrates bearing electron-donating group at different positions were readily reacted with triethylamine, in which steric hindrance and substituting positions have little effect on results (**3a**, **3h** and **3l**; 66%, 63%, and 62% yields). Encouraged by the success of phenylsulfonyl azides, we then exploited the photochemical behaviors of polyaromatic and heteroaromatic sulfonyl azides which provided the corresponding products, **3o** and **3p**, in moderate yields. Gladly, this protocol was also applicable to aliphatic sulfonyl azides, which afforded **3q** and **3r** in 55% and 46% yields, respectively.

Table 1 Optimization of Reaction Conditions[a]



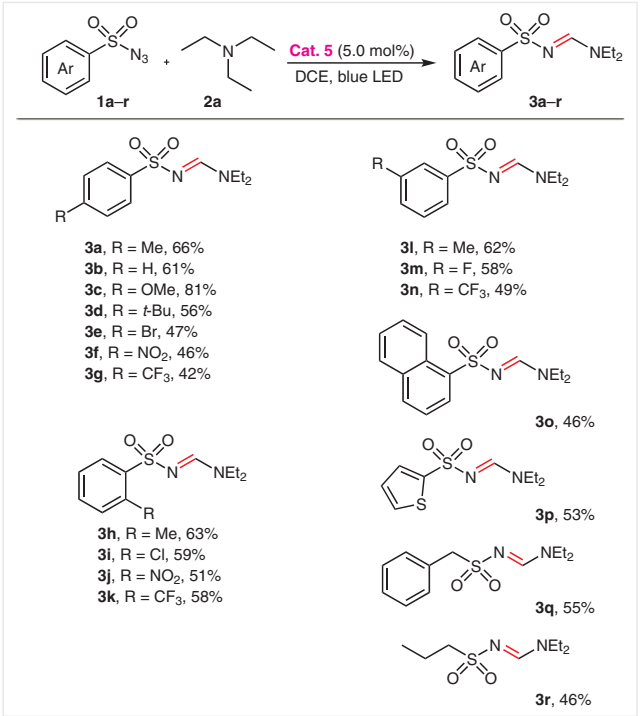


Entry	Photocatalyst	Yield (%)[b]
1	$Ru(bpy)_3Cl_2$	59
2	**cat. 1**	28
3	**cat. 2**	34
4	**cat. 3**	48
5	**cat. 4**	42
6	**cat. 5**	66
7	**cat. 6**	45
8	eosin Y	58
9	rose red	32
10	methyl orange	trace
11	methylene blue	34
12	Congo red	16
13	–	n.d.
14	**cat. 5**, N_2	24
15	**cat. 5**, O_2	67
16	**cat. 5**, in the dark	n.d.

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst (5.0 mol%), DCE (1.0 mL), under air atmosphere.
[b] Isolated yield.

In addition, the reactivity of different amines was further evaluated (Scheme 3). When triethylamine (**2a**) was replaced by tripropylamine (**2b**) and *N*,*N*-diisopropylethylamine (**2c**), the desired products **3s** and **3t** were obtained in 55% and 47% yields, respectively. It is worth noting that when tertiary amines **2d–g** containing a methyl group were employed in this protocol, high site-selectivity for reaction at the methyl group was observed to give sulfonyl amidines in moderate yields. Interestingly, the reactions of **2a**, **2f**, and **2h** afforded same product **3a**, while **2b**, **2g**, and **2i** gave **3s**, indicating three different reaction pathways might be involved in these processes.

In order to demonstrate the synthetic utility of this protocol, gram-scale reaction of **1a** was further carried out under the standard conditions which afforded product **3a** in 71% yield (Scheme 4). Meanwhile, there is no significant



Scheme 2 Scope of sulfonyl azides. *Reagents and conditions*: **1a–r** (0.1 mmol), **2a** (0.3 mmol), **cat. 5** (5.0 mol%), DCE (1.0 mL), under air atmosphere, 12 h; isolated yields are given.

difference in the product yields even if the nitroacenaphthene was recycled for use twelve times, strongly highlighting the economic efficiency of this catalyst (Figure 2).

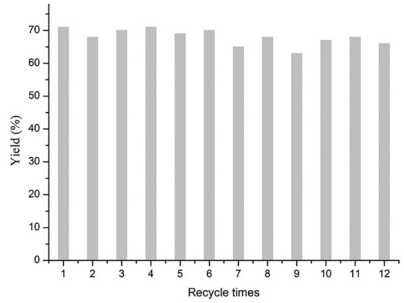
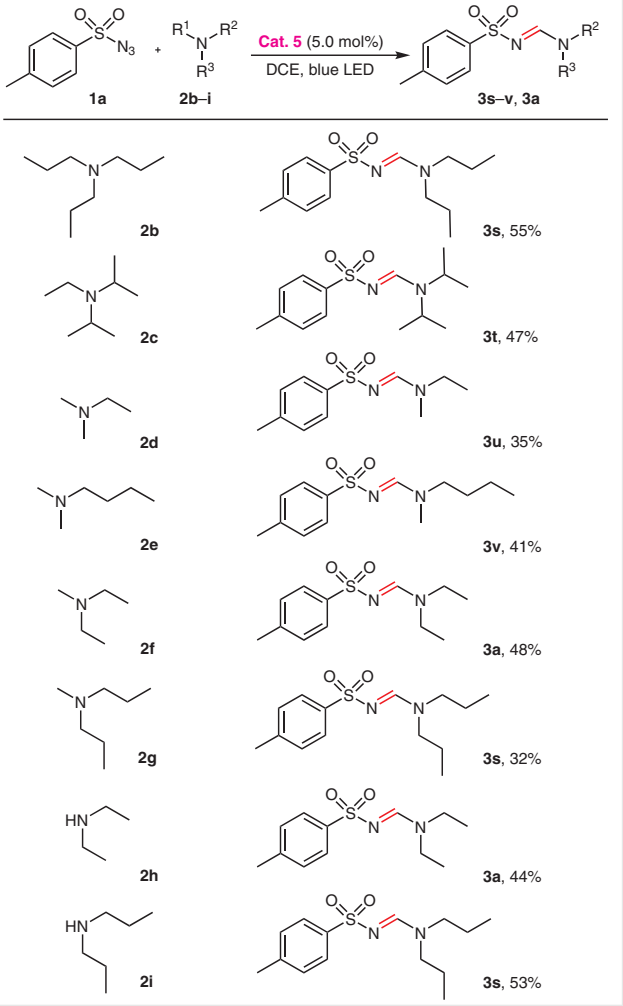
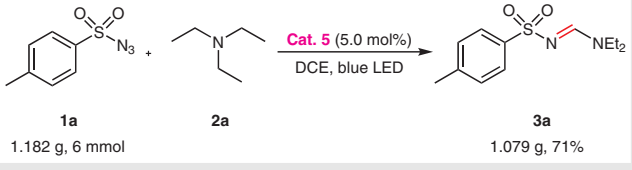


Figure 2 Recycling experiments of **cat. 5**. *Reagents and conditions*: **1a** (3 mmol), **2a** (9 mmol), **cat. 5** (5.0 mol%), DCE (15 mL), under air atmosphere, 15–20 h; isolated yields are given (see Table 2 in the experimental section).

To better understand the mechanisms of this protocol, Stern–Volmer fluorescence quenching experiments were performed. As seen in Figure 3a, the excited catalyst was significantly quenched by triethylamine (**2a**), diethylamine (**2h**) or *N*,*N*-dimethylethylamine (**2d**), which implied the reductive quenching process. This result was also in accordance



Scheme 3 Scope of amines. *Reagents and conditions*: **1a** (0.1 mmol), **2b–i** (0.3 mmol), **cat. 5** (5.0 mol%), DCE (1.0 mL), under air atmosphere, 12 h; isolated yields are given.



Scheme 4 Gram-scale reaction. *Reagents and conditions*: **1a** (6 mmol), **2a** (18 mmol), **cat. 5** (5.0 mol%), DCE (30 mL), under air atmosphere, 20 h; the isolated yield is given.

with cyclic voltammetry test of **cat. 5** ($E_{1/2}(^*PC/PC^-)$ = 1.11 V vs. SCE, Figure 3b),[17] which could accept one electron from triethylamine ($E_{1/2}^{red}$ = 0.85 V vs. SCE in CH_3CN).[18]

Based upon the above experiments and previous relevant reports,[13,19] we proposed two plausible processes according to the different reaction patterns. (1) When each

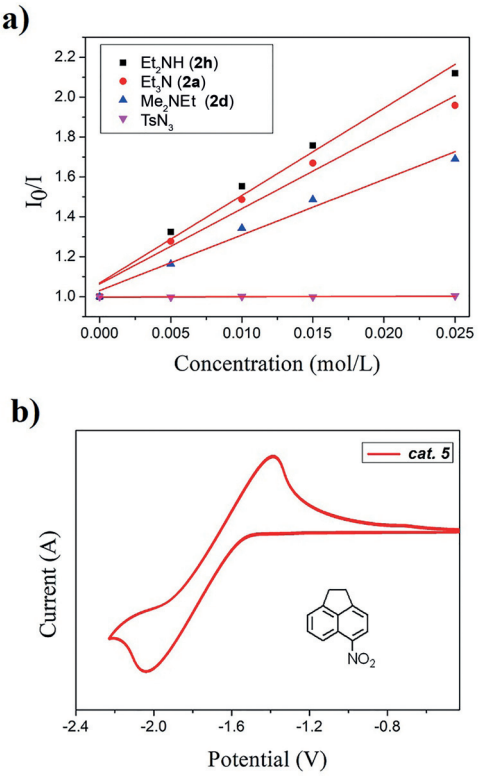
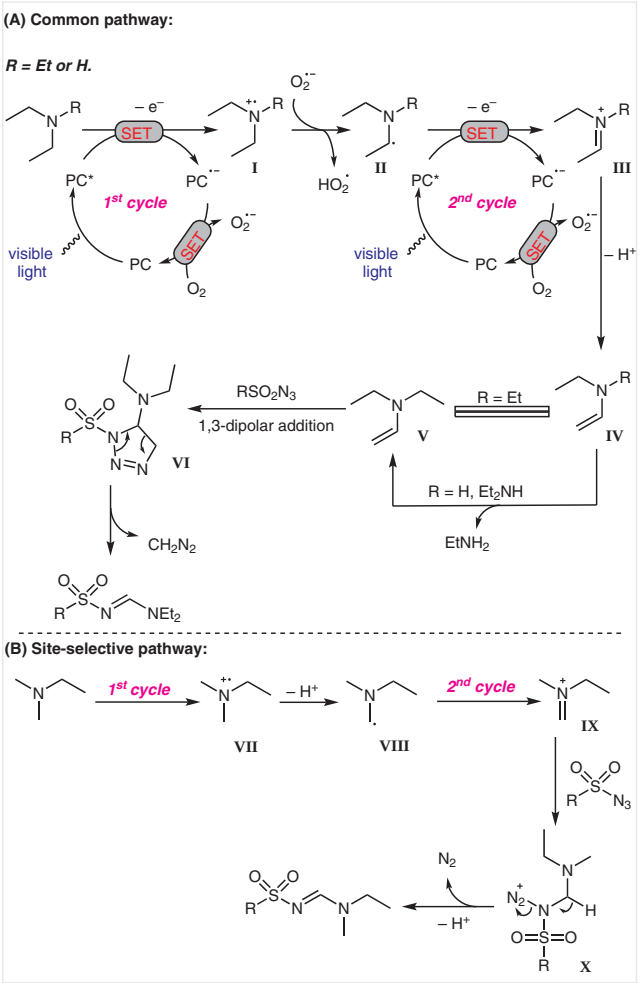


Figure 3 (a) Stern–Volmer fluorescence quenching experiments. (concentration of **cat. 5**: 5.0 × 10^{-3} mol/L in DCE); (b) cyclic voltammogram of **cat. 5** (1.0 mM solution in dry, degassed DCM), Bu_4NPF_6 was used as supporting electrolyte. $E_{1/2}(PC/PC^-)$ = –1.71 V vs. SCE, $E_{1/2}(^*PC/PC^-)$ = 1.11 V vs. SCE.

alkyl chain of the tertiary or secondary amine has more than one carbon, e.g. triethylamine or diethylamine (Scheme 5A), the photoreaction initially proceeds through a single electron transfer (SET) between excited catalyst and triethylamine/diethylamine, the resulting radical cation **I** is further converted into radical **II** by a deprotonation step, and the obtained reduced photocatalyst is then oxidized by O_2. The intermediate **II** is transformed to tertiary enamine **V** through a SET process ($HO_2^•$ could also be an electron acceptor from **II** to form **III**) and deprotonation (in the case of diethylamine, **IV** is proposed to react with Et_2NH to give **V**),[13b] which is then attacked by sulfonyl azide via 1,3-dipolar addition to afford unstable triazoline **VI**. After the release of CH_2N_2, the reaction systems produced the final sulfonyl amine products. (2) When the nitrogen atom of the amine is substituted with a methyl group, the reaction proceeded via another pathway (Scheme 5B). Through the first reductive quenching cycle as depicted in Scheme 5A, the methyl of **VII** undergoes a deprotonation process to give the radical **VIII** due to its greater acidity and lower steric hindrance, which is then reduced to form imine cation **IX**. Subsequently, a series of transformations, including the

nucleophilic addition to the C=N bond by sulfonyl azide,[19] release of N_2, and deprotonation, afford the final sulfonyl amidine products.

In summary, we have developed a small molecule, nitroacenaphthene as a new photocatalyst which could mediate C=N bond formation strategy for the synthesis of sulfonyl amidines. This site-selective protocol displayed a broad substrate scope. Gram-scale and catalyst-recycling experiments have been carried out to demonstrate the potential utility of this catalyst. Further investigation was ongoing to expand its application in other reactions.



Scheme 5 The proposed reaction mechanisms

All the substrates were purchased from Aldrich, Energy Chemical Chemicals, and Aladdin, and all were used as received. ^{1}H NMR (400 MHz or 600 MHz), and ^{13}C NMR (151 MHz) spectra were recorded on Bruker AV-400 instrument in $CDCl_3$ with TMS as internal standard relative to the chemical shift of $CDCl_3$ (δ = 7.26) and for ^{13}C NMR spectra were relative to the center line signal of the $CDCl_3$ triplet (δ = 77.16). HRMS (ESI) spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was performed on a 7890A-5975C/Agilent. Melting points were determined on Buchi B-540. Flash column chromatography was performed using 200–300 mesh silica gel and eluted with petroleum ether (PE)/EtOAc.

Sulfonyl Azides; General Procedure[20]

Sulfonyl chloride (5.0 mmol, 1.0 equiv) was dissolved in acetone (10 mL), NaN_3 (5.5 mmol, 1.1 equiv) was added, and the mixture was stirred at r.t. for 3 h. When the reaction was complete, the aqueous phase was extracted with EtOAc (3 ×), and the combined organic layers were washed with brine and then dried (Na_2SO_4). The solvent was removed under reduced pressure and products were purified by chromatography (silica gel, PE/EtOAc 100:1).

All sulfonyl azides **1a–r** used in experiments were prepared according to this procedure.

N,N-Dialkyl-*N'*-[aryl(or alkyl)sulfonyl]formimidamides 3a–v by Photoreactions; General Procedure

Sulfonyl azide **1a–r** (0.1 mmol), amine **2a–i** (0.3 mmol), and photocatalyst (5.0 mol%) in DCE (1.0 mL) were placed in a glass tube, and the mixture stirred at r.t. under the irradiation of 15-W blue LED until the reaction finished (monitored by TLC). The solvent was removed in vacuo and the residue was purified by column chromatograph (silica gel, PE/EtOAc 5:1–2:1) to afford the product.

Recycling Experiments of Catalyst 5

Compounds **1a** (3 mmol), **2a** (9 mmol), and catalyst **5** (5.0 mol%) in DCE (15.0 mL) were placed in a flask, the mixture stirred at r.t. under the irradiation of 15-W blue LED for 15–20 h. The solvent was removed in vacuo, the residue was purified by column chromatograph (silica gel, PE/EtOAc 50:1) to obtain a mixture of catalyst **5** and unreacted **1a**, and then with PE/EtOAc (5:1) to afford **3a**.

The mixture of catalyst **5** and unreacted **1a** was used in the next cycle.

The yields of **3a** given in Table 2 are isolated yields, which were determined based on compound **1a** (3 mmol and the amount of unreacted **1a** in previous run). The amounts of unreacted **1a** in each run were about 2.6–4.3%, which was determined by GC-MS.

Table 2 Yields of **3a** and the Amount of Unreacted **1a**

Cycle times	**1a** (mmol)	Yield (%) of **3a**	Unreacted (%) **1a**
1	3.00	71	2.6
2	3.08	67	3.1
3	3.09	68	2.9
4	3.09	69	2.8
5	3.08	67	2.8
6	3.09	68	3.1
7	3.09	63	4.2
8	3.13	65	3.3
9	3.10	62	4.3
10	3.13	64	3.6
11	3.11	66	3.4
12	3.10	64	3.7

(*E*)-*N*,*N*-Diethyl-*N*′-tosylformimidamide (3a)[13a]

Eluent: PE/EtOAc (5:1); yield: 16.7 mg (66%) (from Et_3N); 12.2 mg (48%) (from Et_2NMe); 11.2 mg (44%) (from Et_2NH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 7.6 Hz, 2 H), 3.47 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.2 Hz, 2 H), 2.39 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.18, 142.41, 139.88, 129.42, 126.51, 47.17, 41.02, 21.62, 14.65, 12.23.

(*E*)-*N*,*N*-Diethyl-*N*′-(phenylsulfonyl)formimidamide (3b)[13a]

Eluent: PE/EtOAc (5:1); yield: 14.6 mg (61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 2 H), 7.56–7.39 (m, 3 H), 3.47 (q, *J* = 7.2 Hz, 2 H), 3.38 (q, *J* = 7.2 Hz, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.29, 142.71, 131.84, 128.80, 126.44, 47.23, 41.08, 14.62, 12.21.

(*E*)-*N*,*N*-Diethyl-*N*′-(4-methoxyphenylsulfonyl)formimidamide (3c)[13a]

Eluent: PE/EtOAc (5:1); yield: 21.8 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.80 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 3.84 (s, 3 H), 3.46 (q, *J* = 7.2 Hz, 2 H), 3.36 (q, *J* = 7.2 Hz, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.27, 158.00, 134.69, 128.48, 113.94, 55.64, 47.13, 40.97, 14.63, 12.20.

(*E*)-*N*′-(4-*tert*-Butylphenylsulfonyl)-*N*,*N*-diethylformimidamide (3d)[13e]

Eluent: PE/EtOAc (5:1); yield: 16.6 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.79 (d, *J* = 8.6 Hz, 2 H), 7.46 (d, *J* = 8.6 Hz, 2 H), 3.47 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.2 Hz, 2 H), 1.32 (s, 9 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.25, 155.38, 139.74, 126.24, 125.76, 47.13, 40.99, 35.11, 31.23, 14.61, 12.21.

(*E*)-*N*′-(4-Bromophenylsulfonyl)-*N*,*N*-diethylformimidamide (3e)[13f]

Eluent: PE/EtOAc (5:1); yield: 15.0 mg (47%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.74 (d, *J* = 8.6 Hz, 2 H), 7.59 (d, *J* = 8.6 Hz, 2 H), 3.47 (q, *J* = 7.2 Hz, 2 H), 3.38 (q, *J* = 7.2 Hz, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.23, 141.81, 132.03, 128.13, 126.60, 47.33, 41.17, 14.60, 12.20.

(*E*)-*N*,*N*-Diethyl-*N*′-(4-nitrophenylsulfonyl)formimidamide (3f)[13e]

Eluent: PE/EtOAc (5:1); yield: 13.2 mg (46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.9 Hz, 2 H), 8.16 (s, 1 H), 8.06 (d, *J* = 8.9 Hz, 2 H), 3.50 (q, *J* = 7.2 Hz, 2 H), 3.42 (q, *J* = 7.2 Hz, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.44, 149.64, 148.47, 127.81, 124.16, 47.56, 41.42, 14.59, 12.22.

(*E*)-*N*,*N*-Diethyl-*N*′-[4-(trifluoromethyl)phenylsulfonyl]formimidamide (3g)

Eluent: PE/EtOAc (5:1); light yellow oil; yield: 12.9 mg (42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 8.01 (d, *J* = 8.2 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 3.49 (q, *J* = 7.2 Hz, 2 H), 3.40 (q, *J* = 7.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.41, 146.21, 133.58 (q, *J* = 32.8 Hz), 127.04, 125.98 (q, *J* = 3.7 Hz), 123.56 (q, *J* = 272.7 Hz), 47.43, 41.29, 14.60, 12.21.

GC-MS (EI): *m*/*z* = 308.1, 215.1, 145.0, 99.1, 72.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}F_3N_2NaO_2S$: 331.0699; found: 331.0703.

(*E*)-*N*,*N*-Diethyl-*N*′-(*o*-tolylsulfonyl)formimidamide (3h)[13f]

Eluent: PE/EtOAc (5:1); yield: 16.1 mg (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.99 (d, *J* = 7.3 Hz, 1 H), 7.38 (t, *J* = 6.9 Hz, 1 H), 7.26 (t, *J* = 6.9 Hz, 2 H), 3.48 (q, *J* = 7.2 Hz, 2 H), 3.36 (q, *J* = 7.2 Hz, 2 H), 2.69 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.36, 140.78, 137.36, 132.15, 132.02, 127.62, 125.87, 47.16, 41.09, 20.56, 14.65, 12.17.

(*E*)-*N*′-(2-Chlorophenylsulfonyl)-*N*,*N*-diethylformimidamide (3i)[13e]

Eluent: PE/EtOAc (5:1); yield: 16.3 mg (59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1 H), 8.22 (d, *J* = 7.5 Hz, 1 H), 7.48–7.34 (m, 3 H), 3.45 (dq, *J* = 19.3, 7.2 Hz, 4 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.20, 139.25, 133.15, 131.74, 131.49, 130.52, 127.11, 47.35, 41.30, 14.75, 12.16.

(*E*)-*N*,*N*-Diethyl-*N*′-(2-nitrophenylsulfonyl)formimidamide (3j)[13b]

Eluent: PE/EtOAc (5:1); yield: 14.6 mg (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.5 Hz, 1 H), 8.10 (s, 1 H), 7.72–7.60 (m, 3 H), 3.47 (dq, *J* = 11.9, 7.2 Hz, 4 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.01, 147.82, 135.49, 132.86, 132.18, 130.84, 124.14, 47.50, 41.37, 14.52, 12.19.

(*E*)-*N*,*N*-Diethyl-*N*′-[2-(trifluoromethyl)phenylsulfonyl]formimidamide (3k)

Eluent: PE/EtOAc (5:1); light yellow solid; yield: 17.9 mg (58%); mp 60.1–61.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 7.7 Hz, 1 H), 8.17 (s, 1 H), 7.80 (d, *J* = 7.4 Hz, 1 H), 7.65 (dt, *J* = 15.2, 7.1 Hz, 2 H), 3.47 (q, *J* = 7.3 Hz, 2 H), 3.41 (q, *J* = 7.3 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.94, 141.15, 132.35, 132.01, 131.28, 128.01 (q, *J* = 6.4 Hz), 127.32 (q, *J* = 32.9 Hz), 123.13 (q, *J* = 273.5 Hz), 47.22, 41.12, 14.61, 12.10.

GC-MS (EI): *m*/*z* = 308.1, 289.1, 209.1, 145.0, 99.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}F_3N_2NaO_2S$: 331.0699; found: 331.0706.

(*E*)-*N*,*N*-Diethyl-*N*′-(*m*-tolylsulfonyl)formimidamide (3l)[13f]

Eluent: PE/EtOAc (5:1); yield: 15.8 mg (62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.71 (s, 1 H), 7.66 (d, *J* = 7.4 Hz, 1 H), 7.38–7.27 (m, 2 H), 3.47 (q, *J* = 7.2 Hz, 2 H), 3.38 (q, *J* = 7.2 Hz, 2 H), 2.39 (s, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.25, 142.51, 138.88, 132.62, 128.68, 126.89, 123.56, 47.19, 41.04, 21.48, 14.63, 12.21.

(*E*)-*N*,*N*-Diethyl-*N*′-(3-fluorophenylsulfonyl)formimidamide (3m)

Eluent: PE/EtOAc (5:1); light yellow oil; yield: 14.9 mg (58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.68 (d, *J* = 7.9 Hz, 1 H), 7.62–7.53 (m, 1 H), 7.44 (td, *J* = 8.0, 5.4 Hz, 1 H), 7.19 (td, *J* = 8.3, 2.5 Hz, 1 H), 3.49 (q, *J* = 7.2 Hz, 2 H), 3.40 (q, *J* = 7.2 Hz, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.35 (d, *J* = 250.2 Hz), 158.39, 144.77 (d, *J* = 6.7 Hz), 130.59 (d, *J* = 7.7 Hz), 122.24 (d, *J* = 3.3 Hz), 118.99 (d, *J* = 21.2 Hz), 113.94 (d, *J* = 24.3 Hz), 47.36, 41.22, 14.61, 12.21.

GC-MS (EI): *m*/*z* = 258.1, 165.1, 138.1, 99.1, 72.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{15}FN_2NaO_2S$: 281.0730; found: 281.0732.

(*E*)-*N*,*N*-Diethyl-*N*′-[3-(trifluoromethyl)phenylsulfonyl]formimidamide (3n)

Eluent: PE/EtOAc (5:1); light yellow oil; yield: 15.1 mg (49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 3.9 Hz, 2 H), 8.08 (d, *J* = 7.9 Hz, 1 H), 7.76 (d, *J* = 7.8 Hz, 1 H), 7.61 (t, *J* = 7.9 Hz, 1 H), 3.49 (q, *J* = 7.2 Hz, 2 H), 3.41 (q, *J* = 7.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.37, 143.90, 131.37 (q, *J* = 33.3 Hz), 129.82, 129.58, 128.52 (q, *J* = 3.5 Hz), 123.66 (q, *J* = 3.9 Hz), 123.56 (q, *J* = 273.0 Hz), 47.44, 41.30, 14.60, 12.18.

GC-MS (EI): *m*/*z* = 308.1, 289.1, 215.1, 145.0, 99.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}F_3N_2NaO_2S$: 331.0699; found: 331.0705.

(*E*)-*N*,*N*-Diethyl-*N*′-(naphthalen-1-ylsulfonyl)formimidamide (3o)

Eluent: PE/EtOAc (5:1); white solid; yield: 13.3 mg (46%); mp 94.8–97.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 8.6 Hz, 1 H), 8.26 (d, *J* = 7.2 Hz, 1 H), 8.18 (s, 1 H), 7.99 (d, *J* = 8.2 Hz, 1 H), 7.89 (d, *J* = 8.1 Hz, 1 H), 7.64 (t, *J* = 7.3 Hz, 1 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 1 H), 3.44 (q, *J* = 7.2 Hz, 2 H), 3.34 (q, *J* = 7.2 Hz, 2 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.08 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.22, 138.29, 134.29, 133.36, 128.75, 128.61, 127.61, 126.81, 126.65, 126.17, 124.25, 47.25, 41.23, 14.59, 12.09.

GC-MS (EI): *m*/*z* = 290.1, 197.1, 143.0, 127.0, 99.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{18}N_2NaO_2S$: 313.0981; found: 313.0983.

(*E*)-*N*,*N*-Diethyl-*N*′-(thiophen-2-ylsulfonyl)formimidamide (3p)[13b]

Eluent: PE/EtOAc (5:1); yield: 13.1 mg (53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.58 (d, *J* = 3.7 Hz, 1 H), 7.48 (d, *J* = 5.0 Hz, 1 H), 7.12–6.94 (m, 1 H), 3.50 (q, *J* = 7.2 Hz, 2 H), 3.39 (q, *J* = 7.2 Hz, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.17 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.37, 144.32, 130.64, 130.47, 127.02, 47.39, 41.28, 14.62, 12.26.

(*E*)-*N*′-(Benzylsulfonyl)-*N*,*N*-diethylformimidamide (3q)[13e]

Eluent: PE/EtOAc (5:1); yield: 14.0 mg (55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 1 H), 7.38–7.28 (m, 5 H), 4.26 (s, 2 H), 3.43 (q, *J* = 7.2 Hz, 2 H), 3.13 (q, *J* = 7.2 Hz, 2 H), 1.15 (t, *J* = 7.2 Hz, 3 H), 1.04 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.56, 131.08, 130.56, 128.50, 128.35, 59.74, 46.90, 40.95, 14.56, 12.11.

(*E*)-*N*′-(Propylsulfonyl)-*N*,*N*-diethylformimidamide (3r)[13a]

Eluent: PE/EtOAc (5:1); yield: 9.4 mg (46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 3.48 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.2 Hz, 2 H), 3.04–2.91 (m, 2 H), 1.85–1.73 (m, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H), 1.03 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.47, 55.69, 47.05, 40.85, 17.44, 14.55, 13.08, 12.01.

(*E*)-*N*,*N*-Dipropyl-*N*′-tosylformimidamide (3s)[13e]

Eluent: PE/EtOAc (5:1); yield: 15.6 mg (55%); 9.1 mg (32%) (from Pr_2NMe); 14.9 mg (53%) (from Pr_2NH).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 3.35 (t, *J* = 7.4 Hz, 2 H), 3.26 (t, *J* = 7.2 Hz, 2 H), 2.39 (s, 3 H), 1.66–1.60 (m, 2 H), 1.59–1.51 (m, 2 H), 0.90 (t, *J* = 7.4 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.01, 142.34, 139.90, 129.39, 126.45, 54.37, 47.94, 22.01, 21.61, 20.07, 11.33, 10.98.

(*E*)-*N*,*N*-Diisopropyl-*N*′-tosylformimidamide (3t)[13e]

Eluent: PE/EtOAc (5:1); yield: 13.3 mg (47%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 4.62–4.43 (m, 1 H), 3.77–3.58 (m, 1 H), 2.39 (s, 3 H), 1.31 (d, *J* = 6.8 Hz, 6 H), 1.21 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.45, 142.27, 140.06, 129.40, 126.42, 48.57, 48.01, 23.76, 21.61, 19.77.

(*E*/*Z*)-*N*-Ethyl-*N*-methyl-*N*′-tosylformimidamide (3u)

Eluent: PE/EtOAc (5:1), white solid; yield: 8.5 mg (35%); ratio *E*/*Z* 0.65:0.35 (^{1}H NMR); mp 84.6–87.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 0.65 H), 8.09 (s, 0.35 H), 7.75–7.78 (m, 2 H), 7.25 (d, *J* = 6.8 Hz, 2 H), 3.48 (q, *J* = 7.2 Hz, 0.70 H), 3.38 (q, *J* = 7.2 Hz, 1.30 H), 3.08 (s, 1.05 H), 2.98 (s, 1.95 H), 2.39 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 1.95 H), 1.13 (t, *J* = 7.2 Hz, 1.05 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.77, 158.54, 142.56, 142.46, 139.81, 139.70, 129.44, 129.42, 126.63, 126.54, 49.62, 43.14, 38.99, 33.20, 21.62, 13.99, 11.40.

GC-MS (EI): *m*/*z* = 240.1, 147.1, 91.1, 85.1, 65.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{16}N_2NaO_2S$: 263.0825; found: 263.0832.

(*E*/*Z*)-*N*-Butyl-*N*-methyl-*N*′-tosylformimidamide (3v)

Eluent: PE/EtOAc (5:1), white solid; yield: 11.0 mg (41%); ratio *E*/*Z* 0.68:0.32 (^{1}H NMR); mp 96.5–98.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 0.68 H), 8.11 (s, 0.32 H), 7.89–7.63 (m, 2 H), 7.31–7.17 (m, 2 H), 3.43 (t, *J* = 7.6 Hz, 0.64 H), 3.31 (t, *J* = 7.2 Hz, 1.36 H), 3.08 (s, 0.96 H), 2.98 (s, 2.04 H), 2.40 (s, 3 H), 1.59–1.46 (m, 2 H), 1.36–1.21 (m, 2 H), 0.94 (t, *J* = 7.3 Hz, 2.04 H), 0.88 (t, *J* = 7.4 Hz, 0.96 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.15, 158.89, 142.55, 142.42, 139.84, 139.72, 129.45, 129.38, 126.62, 126.51, 54.68, 48.01, 39.57, 33.69, 30.18, 28.20, 21.63, 19.91, 19.62, 13.81, 13.72.

GC-MS (EI): *m*/*z* = 268.1, 253.1, 147.1, 113.1, 91.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{20}N_2NaO_2S$: 291.1138; found: 291.1143.

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Supporting Information

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