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## Graphical Abstract

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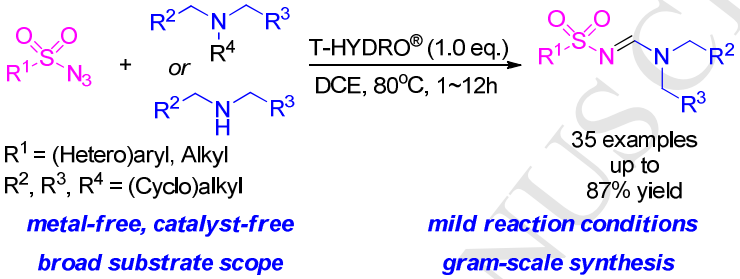


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# Synthesis of *N*-Sulfonylformamidines by *tert*-Butyl Hydroperoxide–Promoted, Metal-Free, Direct Oxidative Dehydrogenation of Aliphatic Amines

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ABSTRACT

A direct and convenient metal-free method to prepare sulfonyl amidines in the presence of aqueous *tert*-butyl hydroperoxide (T-HYDRO) has been developed. Different tertiary and secondary amines were tested for compatibility with the oxidative conditions and could be coupled with sulfonyl azides to form the corresponding amidines in moderate to good yields.

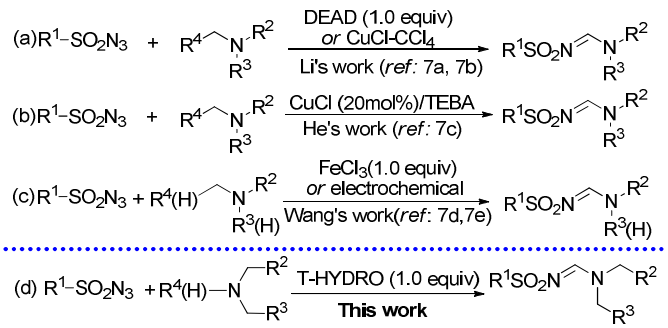


## 1. Introduction

Amidines are interesting compounds because they have a unique structural motif, and are regarded as organic superbases,1 as well as being key intermediates in the synthesis of heterocyclic compounds,[2] and versatile nitrogen ligands in metallocyclic complexes.[3] Amidines are also important in medicinal chemistry because they are found in many bioactive natural products[4] and have been identified as important pharmacophores.[5]

There are several well-known practical methods for the synthesis of *N*-sulfonyl formamidines[6] and recent efforts have been dedicated to the improvement of traditional protocols.[7] Among selected elegant examples, the Li group have reported two types of dehydrogenation of aliphatic tertiary amines: using sulfonyl azides in the presence of stoichiometric diethyl azodicarboxylate (DEAD)[7a] and CuCl-$CCl_4$[7b] catalytic systems (Scheme 1, eq a). He and co-workers have also reported the CuCl-catalyzed imidation of a tertiary amine using sulfonyl azides as the nitrogen source in the presence of benzyltriethylammonium chloride (TEBA)[7c] (Scheme 1, eq b). Wang and co-workers have developed a synthesis of sulfonyl amidines from tertiary amines and sulfonyl azides in the presence of a stoichiometric amount of $FeCl_3$[7d], as well as an electrochemical approach[7e] (Scheme 1, eq c). Although tremendous efforts have been made,[6g] a milder and metal-free method for the synthesis of sulfonyl amidines is still in demand.

Various synthetic methodologies have been developed for activation/ functionalization of the α, β-C($sp^3$)-H bonds of amines. However, most of these procedures need a transition metal as the active catalyst.[8] Thus, the development of a new and efficient metal-free method for the simultaneous oxidative dehydrogenation and functionalization of amines remains a significant challenge. Based on our previous work on oxidation using *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant,[9] we investigated the use of TBHP for the oxidative dehydrogenation of amines. Herein, we describe a mild and simple T-HYDRO (TBHP 70 wt% in water)-promoted, catalyst-free direct functionalization of aliphatic amines with sulfonyl azides to produce sulfonyl formamidines (Scheme 1, eq d).




**Scheme 1.** Representative approaches for synthesis of *N*-sulfonylformamidines

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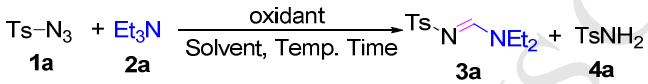
## 2. Results and Discussion

Initially, we chose tosylazide ($TsN_3$) **1a** and triethylamine **2a** as standard substrates to optimize suitable conditions for this reaction (Table 1). To our delight, the reaction of **1a** (1.2 equiv.) with **2a** (1.0 equiv.) was performed smoothly in the presence of 2.0 equiv. of T-HYDRO in ethyl acetate (EtOAc) at 60 °C, and generated the desired sulfonyl formamidine **3a** in 40% yield, while the tosylamide **4a** was also isolated as a byproduct in approximately 20% yield (entry 1). Therefore, we investigated the use of an excess of $TsN_3$. As expected, when the amount **1a** was increased from 1.2 to 2.0 and 2.5 equiv. the yield of **3a** was gradually increased to 55% and 60%, respectively and the yield of the isolated tosylamide **4a** to 40% (entries 2–3). Various solvents, including acetonitrile (MeCN), chloroform ($CHCl_3$), dichloromethane (DCM), and 1,2-dichloroethane (DCE) were screened (entries 4–7). The highest yield was observed with DCE (entry 7). A 75% yield was also obtained by raising the reaction temperature to 80 °C and shortening the reaction time from 24 to 5 h (entry 8). Surprisingly, when treated with 3.0 equiv. of T-HYDRO, **1a** was consumed in 2 h and the yield of **3a** decreased to 60% (entry 9). In contrast, the use of 1.0 equiv. of T-HYDRO generated a 77% yield of product (entry 10). The use of TBHP in decane instead of T-HYDRO gave a similar yield of the product (entry 11). Leaving the other conditions unchanged and decreasing the loading of $TsN_3$ to 2.0 equiv. resulted in the highest yield of 78% (entry 12). Further screening of different oxidants revealed no better results (entries 13–16). Moreover, the yield of **3a** showed an obvious decline when the amount of $TsN_3$ was decreased (entry 17). When the molar ratio of **1a** : **2a** was changed to from 2:1 to 1:3, the yield decreased (entry 18). Interestingly, a 6.0% yield of the desired sulfonyl amidine **3a** could be isolated in the absence of T-HYDRO (entry 19). Therefore, the optimal reaction conditions were determined to be treatment of sulfonylazide (**1**) with tertiary amine (**2**) in a 2:1 molar ratio, with T-HYDRO (1.0 equiv.) as the oxidant, in DCE at 80 °C.

**Table 1.** Optimizing the condition for the formation of **3a** [a]

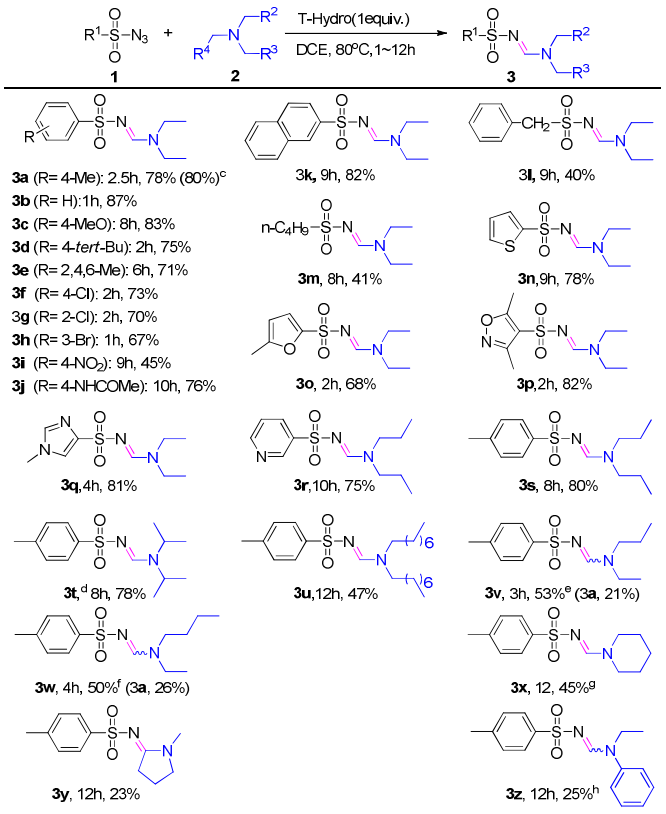



| Entry | 1a: 2a | Oxidant (eq.) | Solvent | Temp. (°C) | Time (h) | Yield of 3a (%)[b] |
|---|---|---|---|---|---|---|
| 1 | 1.2 : 1 | T-HYDRO (2) | EtOAc | 60 | 2 | 40 |
| 2 | 2.0 : 1 | T-HYDRO (2) | EtOAc | 60 | 4 | 55 |
| 3 | 2.5 : 1 | T-HYDRO (2) | EtOAc | 60 | 24 | 60 |
| 4 | 2.5 : 1 | T-HYDRO (2) | MeCN | 60 | 24 | 55 |
| 5 | 2.5 : 1 | T-HYDRO (2) | $CHCl_3$ | 60 | 24 | 20 |
| 6 | 2.5 : 1 | T-HYDRO (2) | DCM | 60 | 24 | 56 |
| 7 | 2.5 : 1 | T-HYDRO (2) | DCE | 60 | 24 | 65 |
| 8 | 2.5 : 1 | T-HYDRO (2) | DCE | 80 | 5 | 75 |
| 9 | 2.5 : 1 | T-HYDRO (3) | DCE | 80 | 2 | 60 |
| 10 | 2.5 : 1 | T-HYDRO (1) | DCE | 80 | 5 | 77 |
| 11[c] | 2.5 : 1 | TBHP (1) | DCE | 80 | 5 | 77 |
| **12** | **2.0 : 1** | T-HYDRO (1) | **DCE** | **80** | **2.5** | **78** |
| 13 | 2.0 : 1 | DTBP (1) | DCE | 80 | 8 | 8 |
| 14 | 2.0 : 1 | CHP (1) | DCE | 80 | 5 | 63 |
| 15 | 2.0 : 1 | TBPB (1) | DCE | 80 | 8 | 30 |
| 16 | 2.0 : 1 | BPO (1) | DCE | 80 | 8 | 48 |
| 17 | 1.5 : 1 | T-HYDRO (1) | DCE | 80 | 1 | 55 |
| 18 | 1 : 3.0 | T-HYDRO (1) | DCE | 80 | 1 | 30 |
| 19 | 2.0 : 1 | - | DCE | 80 | 12 | 6 |

[a] Reactions were performed in 2 mL of solvent in a sealed tube unless otherwise noted. [T-HYDRO]: TBHP, 70 wt% in water. [DTBP]: Di-*tert*-butylperoxide. [CHP]: Cumyl hydroperoxide. [TBPB]: *tert*-Butyl peroxybenzoate. [BPO]: Benzoyl peroxide. [b] Isolated yield after column chromatography. [c] TBHP 5.5 M in decane.

With the optimized conditions in hand, the scope of the reaction was investigated as shown in Table 2. A wide range of sulfonyl azides and tertiary amines could be used in this reaction system under the optimized conditions. The phenylsulfonyl azides bearing electron-donating and electron-withdrawing groups reacted with triethylamine to afford the corresponding sulfonyl amidines in good to excellent yields (Table 2, **3a**−**3j**). Moreover, having the substituted group at different positions on the phenyl ring had no obvious effect on the reaction. However, the strong electron-withdrawing nitro group gave a comparably lower yield of **3i**. 2-Naphthalenesulfonyl azide reacted slowly, but the desired product **3k** was obtained in a relatively high yield. Notably, the aliphatic sulfonylazides, benzylsulfonyl azide and butylsulfonyl azide, afforded the products **3l** and **3m** in nearly 40% isolated yields. In addition, the five membered heteroaromatic sulfonyl azide derivatives with one or two heteroatoms provided the corresponding amidines in good yields (Table 2, **3n**−**3q**). Furthermore, the reaction of 3-pyridinesulfonyl azide with *tri*-propyl amine allowed the formation of the **3r** in 75% yield. To our satisfaction, an array of tertiary amines proved to be suitable reaction partners and afforded the corresponding coupling

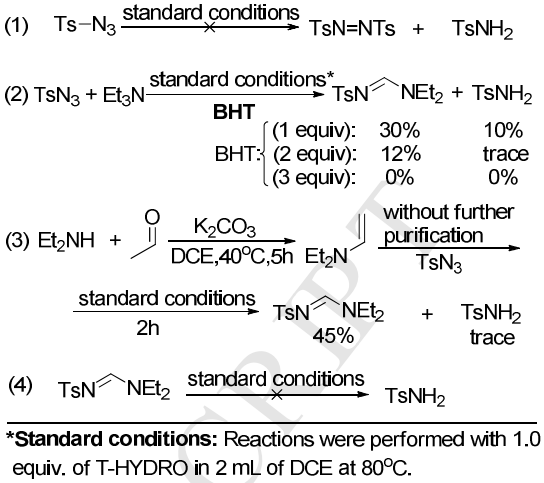
**Table 2.** Scope of sulfonyl azides and tertiary amines[a,b]




[a] Reactions were performed with 2.0 mmol of sulfonyl azide **1** (2.0 equiv.), 1.0 mmol of tertiary amine **2** (1.0 equiv.) and 1.0 mmol of T-HYDRO (1.0 equiv.) in 2 mL of DCE, unless otherwise noted. [b] Isolated yield after column chromatography. [c] Gram scale reaction in 5 h. [d] *N*,*N*-diisopropylethylamine was used. [e] The ratio of E/Z isomers was 4:3. [f] The ratio of E/Z isomers was 4:3. [g] 2.0 Equiv. of T-HYDRO was used. [h] The ratio of E/Z isomers was 4:1.

products **3s–3w** in good to moderate yields. For *tri*-n-octylamine, the yield of corresponding sulfonyl amidine **3u** was 47%, probably because of steric hindrance from the long alkyl group. Tertiary amines with different alkyl groups, *N*,*N*-diethylpropylamine and *N*,*N*-diethylbutylamine, were also investigated and two products (**3v/3a** and **3w/3a**) were obtained for each tertiary amine in good yields, and it was found that the reaction was more selective for the ethyl group giving a ratio for the two products of nearly 2:1. Cyclic amines were also used as substrates and *N*-ethyl piperidine produced the corresponding amidine **3x** in 45% isolated yield with a trace amount of product resulting from hydrogen abstraction from the cyclic α-carbon. Interestingly, when using *N*-methylpyrrolidine, the cyclic sulfonyl amidine **3y** was obtained predominantly. The aromatic tertiary amine *N*,*N*-diethyl aniline gave a relatively poor yield of **3z** with a mixture of E and Z configurations.

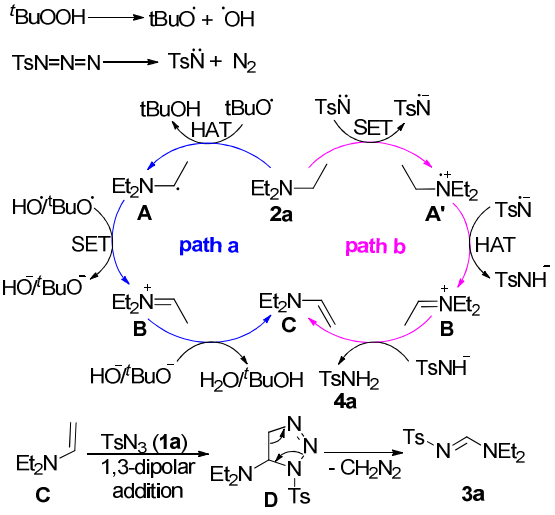
To gain further insight into the mechanism of the reaction, a series of control experiments were carried out (Scheme 2). First, tosylazide and T-HYDRO were reacted under the standard reaction conditions; however, neither sulfonamide nor 1,2-ditosyldiazene (TsN=NTs)[7c] were observed (Scheme 2, eq. 1). Then, butylated hydroxytoluene (BHT) as a radical scavenger[10] was added to the reaction mixture. When 1.0 or 2.0 equiv. BHT was used, the yields of product and sulfonamide decreased dramatically, and no products were obtained when 3.0 equiv. of BHT were used and the starting material **1a** was almost completely recovered (Scheme 2, eq. 2). From these results, we believe that a radical pathway is involved in the reaction process. In addition, we considered that the enamine may be the intermediate product, and to confirm this hypothesis, *N*,*N*-diethylethenamine was synthesized via the reaction of diethylamine with acetaldehyde using $K_2CO_3$ as the dehydrating agent,[11] followed by reaction with **1a** without further purification to give **3a** isolated in 45% yield (Scheme 2, eq. 3). Furthermore, the enamine intermediate was also successfully captured using




**Scheme 2.** Control experiments

(2,4-dinitrophenyl)hydrazine [see Electronic Supporting Information (ESI)]. However, the sulfonyl amidine could not be converted to the sulfonamide under the standard conditions (Scheme 2, eq. 4).

Combined with literature reports[7a–d] and the aforementioned experimental results, a plausible mechanism for this coupling reaction is proposed in Scheme 3. The sulfonyl azide and *tert*-butyl hydroperoxide system exhibits mutually-induced decomposition[12] and homolytic cleavage of TBHP produces the alkoxyl and hydroxyl radicals.[13] The decomposition of sulfonyl azide gives sulfonylnitrene and nitrogen.[14] We envisioned that the enamine may be the key intermediate in this system and two possible pathways may be involved: a) an alkoxy radical-promoted mechanism; and b) a sulfonyl nitrene-promoted mechanism. In path a, the initial step begins with the alkoxyl radical then hydrogen is abstracted from the tertiary amine to generate radical **A**, this is followed by an electron transfer to form the iminium ion **B**.[15] Subsequently, **B** is converted into enamine **C** by further deprotonation. The nitrene promoted pathway (path b) is also possible for this reaction.[16] First, the cation radical **A'** is formed from the tertiary amine and sulfonyl

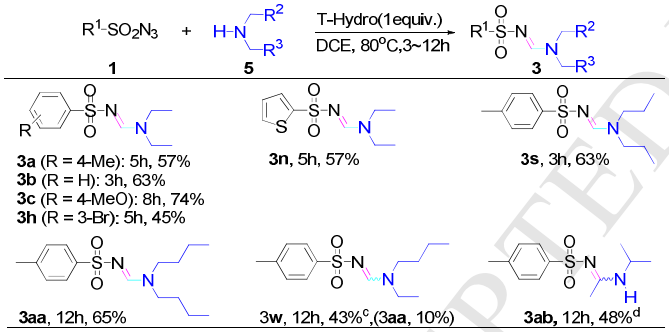



**Scheme 3.** Possible reaction mechanism

nitrene, while a nitrene radical anion is also formed by a SET, which is followed by sequential H-atom transfer and deprotonation to form the iminium ion **B** and enamine **C**, while the sulfonamide **4a** is formed as a byproduct. Finally, The triazoline intermediate **D** is produced from enamine **C** and $TsN_3$ through a 1,3-dipolar cycloaddition reaction, and the subsequent release of one molecule of diazomethane[17] affords the final product **3a**.

The current direct dehydrogenative functionalization was further extended to secondary amines using the developed reaction conditions. Interestingly, we observed that a wide array of sulfonyl azides and secondary amine derivatives were well tolerated and the same products were obtained as found for the tertiary amines (Table 3). Aromatic sulfonyl azides reacted with diethylamine smoothly and afforded the corresponding products (**3a–c, 3h** and **3n**) in 45%–74% yields. It is noteworthy that di-n-propylamine and di-n-butylamine can be transformed into their corresponding amidines **3s** and **3aa** in 53- 65% yield respectively. When *N*-ethylbutylamine was used as reaction partner, two products (**3w** and **3aa**) were isolated in a 4:1 ratio. These results indicate that secondary amine is oxidized to form secondary enamine through the same route as tertiary amine, then enamine exchanges with one molecule of secondary amine to give tertiary enamine.[18] Surprisingly, when diisopropylamine was used as a reactant, a different type of sulfonyl amidine **3ab** was isolated in 48% yield as a mixture of Z and E isomers. This result revealed that the sterically hindered diisopropylamine is directly oxidized to form the secondary enamine, and then the reaction follows the same route as for tertiary amines, (details are provided in the ESI).

**Table 3.** Reaction of sulfonyl azides with secondary amines[a,b]




[a] Reactions were performed with 2.0 mmol of sulfonyl azide **1** (1.0 equiv.), 1.0 mmol of secondary amine **2** (1.0 equiv.) and 1.0 mmol of T-HYDRO (1.0 equiv.) in 2 mL of DCE, unless otherwise noted. [b] Isolated yield after column chromatography. [c] The ratio of E/Z isomers was 4:3. [d] The ratio of E/Z isomers was 2:1.

Then, we investigated whether primary amines could tolerate this transformation; however, the application of primary amines was not successful.

## 3. Conclusions

We have developed a novel metal-free protocol for the synthesis of sulfonyl amidines from aliphatic amines and sulfonyl azides in the presence of aqueous tert-butyl hydroperoxide. This method was employed for different tertiary and secondary amines and the corresponding amidines were generated in moderate to high yield. Several control experiments were conducted and potential mechanisms were proposed. The oxidative dehydrogenation of the α, β-C($sp^3$)-H bond of an aliphatic amine to form an enamine is a key step to give the desired products. Further research on elucidating the oxidative mechanism of TBHP with tertiary amines and synthetic applications of the strategy are in progress in our lab.

## 4. Experimental Section

### *4.1. General information*

Substituted sulfonyl azides were prepared according to the literature.[19] (*Caution: Azides may be hazardous and/or explosive.*) $Et_3N$ was distilled from sodium/benzophenone. Other reagents and solvents were obtained from commercial available and used directly without further purification. T-HYDRO was purchased from Alfa as a 70 wt% aqueous solution. Purification of the reaction products was carried out by flash column chromatography using 200–300 mesh silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid or anisaldehyde stain followed by heating. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian spectrometer in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-$d_6$) with the solvent residual peak as an internal reference unless otherwise stated ($CDCl_3$: $^1H$ = 7.26 ppm, $^{13}C$ = 77.16 ppm; DMSO-$d_6$: $^1H$ = 2.50 ppm, $^{13}C$ = 39.52 ppm). $^1H$ NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), coupling constant(s) in Hz, integration. High-resolution mass spectra were recorded on a Bruker BIO TOF Q mass spectrometer.

### *4.2. General procedure for the synthesis of compounds 3*

To a 5-mL screw-cap vial containing sulfonyl azide (2.0 mmol) and tertiary amine or secondary amine (1.0 mmol) in 2.0 mL of DCE, was added T-HYDRO (70 wt% in $H_2O$, 1.0 equiv.) in a single delivery via syringe. The vial was tightly capped and the reaction mixture was stirred at 80 °C for the indicated time (monitored by TLC). After the reaction was completed, the solvent was removed under reduced pressure. The crude residue was purified via silica gel column chromatography with an appropriate eluting solvent system (ethyl acetate- petroleum ether).

*4.2.1. (E)-N,N-diethyl-N'-tosylformimidamide* (**3a**):[7a] White solid, mp: 71–72 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.46 (q, *J* = 7.2 Hz, 2H), 3.37 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 158.1, 142.3, 139.9, 129.3, 126.4, 47.1, 41.0, 21.5, 14.6, 12.2.

*4.2.2. (E)-N,N-diethyl-N'-(phenylsulfonyl)formimidamide* (**3b**):[7a] White solid, mp: 76–77 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.48-7.42 (m, 3H), 3.46(q, *J* = 7.2 Hz, 2H), 3.36 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 158.2, 142.7, 131.7, 128.7, 126.4, 47.2, 41.0, 14.5, 12.18.

*4.2.3 . (E)-N,N-diethyl-N'-((4-methoxyphenyl)sulfonyl)formimid-amide* (**3c**):[7a] White solid, mp: 64–65 °C. $^1H$ NMR (400MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3 H), 3.44 (q, *J* = 7.2 Hz, 2H), 3.35 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 162.2, 157.9, 134.7, 128.4, 113.9, 55.6, 47.1, 40.9, 14.5, 12.1.

*4.2.4. (E)-N'-((4-(tert-butyl)phenyl)sulfonyl)-N,N-diethylformimid amide* (**3d**): White solid, mp: 95–96 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H) , 3.47 (q, *J* = 7.2 Hz, 2H), 3.37 (q, *J* = 7.2 Hz, 2H), 1.31 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 158.2, 155.3, 139.7, 126.2, 125.7, 47.1, 41.0, 35.1, 31.2, 29.7, 14.6, 12.2. HRMS calcd. for $C_{15}H_{24}N_2NaO_2S$ $[M+Na]^+$; 319.1456; found 319.1461.

*4.2.5. (E)-N,N-diethyl-N'-(mesitylsulfonyl)formimidamide* (**3e**):[7a] White solid, mp: 77–78 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1H), 6.90 (s, 1H) , 3.45 (q, *J* = 7.2 Hz, 2H), 2.67 (s, 6H), 2.27 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.14(t, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ =157.5, 141.2, 138.5, 136.7, 131.5, 46.9, 40.9, 23.1, 21.0, 14.7, 14.2.

*4.2.6. (E)-N'-((4-chlorophenyl)sulfonyl)-N,N-diethylformimidamide* (**3f**):[7a] White solid, mp: 86–87 °C. $^1$H NMR (400MHz, $CDCl_3$): δ = 8.12 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H),7.41 (d, *J* = 8.4 Hz, 2H), 3.46 (q, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.2, 141.3, 138.1,129.0, 127.9, 47.3, 41.1, 14.5, 12.1.

*4.2.7. (E)-N'-((2-chlorophenyl)sulfonyl)-N,N-diethylformimidamide* (**3g**): White solid, mp: 82–83 °C. $^1$H NMR (400MHz, DMSO-$d_6$): δ = 8.28 (s, 1H), 8.04 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.60 (dd, *J* = 4.8, 0.6 Hz, 2H), 7.53-7.49 (m, 1H), 3.53 (q, *J* = 7.2 Hz, 2H), 3.36 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 160.0, 139.4, 133.5, 131.5, 130.5, 129.4, 127.5, 46.4, 40.5, 14.4, 11.7; HRMS calcd. for $C_{11}H_{15}ClN_2NaO_2S$ $[M+Na]^+$; 297.0440; found 297.0438.

*4.2.8. (E)-N'-((3-bromophenyl)sulfonyl)-N,N-diethylformimidamide* (**3h**): White solid, mp: 79–80 °C. $^1$H NMR (400MHz, DMSO-$d_6$): δ = 8.24 (s, 1H), 7.90 (s, 1H), 7.89-7.76 (m, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 3.49 (q, *J* = 7.2 Hz, 2H), 3.36 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 159.2, 145.1, 134.5, 131.3, 128.2, 124.9, 121.8, 46.4, 40.4, 14.1, 11.8; HRMS calcd. for $C_{11}H_{15}BrN_2NaO_2S$ $[M+Na]^+$; 340.9935; found 340.9939.

*4.2.9. (E)-N,N-diethyl-N'-((4-nitrophenyl)sulfonyl)formimidamide* (**3i**):[7d] $^1$H NMR (400MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.8 Hz 2H), 8.15 (s, 1H) 8.05 (d, *J* = 9.2 Hz, 2H), 3.49 (q, *J* = 7.2 Hz, 2H), 3.42 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.4, 149.6, 148.5,127.8, 124.4, 47.5, 41.4, 14.5, 12.2.

*4.2.10. (E)-N-(4-(N-((diethylamino)methylene)sulfamoyl)phenyl)-acetamide* (**3j**): White solid, mp: 101–102 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 10.53 (bs, 1H), 8.17(s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H) , 3.46 (q, *J* = 7.2 Hz, 2H), 3.35 (q, *J* = 7.2 Hz, 2H), 2.08 (s, 3H),1.14 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 168.9, 158.5, 142.2, 136.8, 126.7, 118.3, 46.2, 24.1, 24.0, 14.3, 11.8; HRMS calcd. for $C_{13}H_{19}N_3NaO_3S$ $[M+Na]^+$; 320.1045; found 320.1049.

*4.2.11. (E)-N,N-diethyl-N'-(naphthalen-2-ylsulfonyl)formimidamide* (**3k**):[7a] White solid, mp: 99–100 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.20 (s, 1H), 7.95-7.85 (m, 4H), 7.60-7.56 (m, 2H) , 3.48(q, *J* = 7.2 Hz, 2H), 3.39 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.3, 139.6, 134.6, 132.3, 129.3, 129.0, 128.3, 127.9, 127.2, 127.0, 122.6, 47.2, 41.1, 14.6, 12.2.

*4.2.12. (E)-N'-(benzylsulfonyl)-N,N-diethylformimidamide* (**3l**) : White solid, mp: 80–81 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.56 (s, 1H), 7.31 (m, 5H), 4.26(s, 2H), 3.35(q, *J* = 7.2 Hz, 2H), 3.28 (q, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 159.3, 130.9, 130.8, 128.0, 127.7, 59.0, 46.0, 14.2, 11.6; HRMS calcd. for $C_{12}H_{18}N_2NaO_2S$ $[M+Na]^+$; 277.0987; found 277.0984.

*4.2.13. (E)-N'-(butylsulfonyl)-N,N-diethylformimidamide* (**3m**):[7a] Light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 3.48 (q, *J* = 7.2 Hz, 2H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 8.0 Hz, 2H), 1.79-171 (m, 2H), 1.46-1.40 (m, 2H), 1.26 (q, *J* = 7.2 Hz, 3H), 1.19 (d, *J* = 7.2 Hz, 3H), 0.92(t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.4, 53.7, 47.1, 40.9, 25.8, 21.7, 14.6, 13.7, 12.1.

*4.2.14. (E)-N,N-diethyl-N'-(thiophen-2-ylsulfonyl)formimidamide* (**3n**):[7a] White solid, mp: 56–57 °C.$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.21 (s, 1H), 7.82 (d, *J* = 4.0 Hz, 1H), 7.50 (d, *J* = 4.0 Hz, 1H), 7.10 (t, *J* = 4.0 Hz, 1H) , 3.49 (q, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 158.8, 144.7, 131.4, 129.9, 127.3, 46.5, 14.2, 11.9.

*4.2.15. (E)-N,N-diethyl-N'-((5-methylfuran-2-yl)sulfonyl)formimidamide* (**3o**): Viscous liquid. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1H), 8.51 (d, *J* = 3.2 Hz, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 3.50(q, *J* = 7.2 Hz, 2H), 3.40 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.1, 156.1, 148.8, 115.5, 107.3, 47.3, 41.2, 14.5, 13.9, 12.1; HRMS calcd. for $C_{10}H_{16}N_2NaO_3S$ $[M+Na]^+$; 267.0779; found 267. 0774.

*4.2.16. (E)-N'-((3,5-dimethylisoxazol-4-yl)sulfonyl)-N,N-diethylformimidamide* (**3p**): Waxy solid. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 3.46 (q, *J* = 7.2 Hz, 2H), 3.39 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.37 (s, 3H), 1.26 (t , *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 170.8, 157.8, 157.7, 118.7, 47.2, 41.1, 14.5, 12.6, 12.0, 11.0; HRMS calcd. for $C_{10}H_{17}N_3NaO_3S$ $[M+Na]^+$; 282.0888; found 282. 0885.

*4.2.17. (E)-N,N-diethyl-N'-((1-methyl-1H-imidazol-4-yl)sulfonyl)-formimidamide* (**3q**): White solid, mp: 91–92 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 7.49 (s, 1H), 7.48 (s, 1H), 3.72 (s, 3H), 3.48 (q, *J* = 7.2 Hz, 2H), 3.41 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.7, 142.5, 138.6, 122.9, 47.2, 40.9, 34.1, 14.5, 12.1; HRMS calcd. for $C_9H_{16}N_4NaO_2S$ $[M+Na]^+$; 267.0892; found 267. 0889.

*4.2.18. (E)-N,N-dipropyl-N'-(pyridin-3-ylsulfonyl)formimidamide* (**3r**): White solid, mp: 93–94 °C. $^1$H NMR (600 MHz, $CDCl_3$): δ = 9.06 (s, 1H), 8.72 (d, *J* = 4.8 Hz, 1H), 8.18-8.16 (m, 2H), 7.40(dd, *J* = 4.8, 3.0 Hz, 1H), 3.38 (t, *J* = 7.8 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H), 1.67-1.57 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.87(t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 159.2, 152.4, 147.6, 139.3, 134.1, 123.5, 54.6, 48.2, 22.0, 20.1, 11.3, 11.0; HRMS calcd. for $C_{12}H_{19}N_3NaO_2S$ $[M+Na]^+$; 292.1096; found 292.1094.

*4.2.19. (E)-N,N-dipropyl-N'-tosylformimidamide* (**3s**):[7d] White solid, mp: 43–44 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.35 (t, *J* = 7.6 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.65-1.54 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H),; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.0, 142.3, 139.9, 129.3, 126.4, 54.3, 47.9, 22.0, 21.6, 20.1, 11.3, 10.9.

*4.2.20. (E)-N,N-diisopropyl-N'-tosylformimidamide* (**3t**) :[7b] White solid, mp: 110–111 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.23(d, *J* = 8.4 Hz, 2H), 4.55-4.48 (m, 1H), 3.70-3.63 (m, 1H), 2.38 (s, 3H), 1.30 (d, *J* = 6.8 Hz,6H), 1.20 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ =156.2, 142.0, 139.9, 129.2, 126.2, 48.4, 47.8, 23.5, 21.4, 19.6.

*4.2.21. (E)-N,N-dioctyl-N'-tosylformimidamide* (**3u**): viscous oil. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.19 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 3.41 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.53-1.42 (m, 4H), 1.27-1.15 (m, 20H), 0.87-0.82 (m, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ =

159.5, 141.8, 140.3, 129.2, 125.7, 51.3, 31.1, 28.59, 28.54, 28.46, 25.98, 22.04, 13.92; HRMS calcd. for $C_{24}H_{42}N_2NaO_2S$ $[M+Na]^+$; 445.2865; found 445.2864.

*4.2.22. (E/Z) N-ethyl-N-propyl-N'-tosylformimidamide* (**3v**): White solid, mp: 62–63 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 0.4H), 8.10 (s, 0.6H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.44 (q, *J* = 7.2 Hz, 1.2H), 3.35 (q, *J* = 7.2 Hz, 1.7H), 3.25 (t, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 1.64-1.53 (m, 2H), 1.23(t, *J* = 7.2 Hz, 1.4H), 1.12(t, *J* = 7.2 Hz, 1.6H), 0.91 (t, *J* = 7.2 Hz, 1.7H), 0.86 (t, *J* = 7.2 Hz, 1.3H),; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.6, 158.5, 142.33, 142.31, 139.9, 129.36, 129.34, 126.4, 54.0, 47.6, 47.4, 41.3, 22.0, 21.5, 20.1, 14.6, 12.1, 11.3, 10.9; HRMS calcd. for $C_{13}H_{20}N_2NaO_2S$ $[M+Na]^+$; 291.1143; found 291.1144.

*4.2.23. (E/Z) N-butyl-N-ethyl-N'-tosylformimidamide* (**3w**): White solid, mp: 54–55 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 0.4H), 8.09 (s, 0.6H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.45-3.31 (m, 3H), 3.27 (q, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 1.57-1.47 (m, 2H), 1.31-1.20(m, 3.5), 1.23(t, *J* = 7.2 Hz, 1.4H), 1.10(t, *J* = 7.2 Hz, 1.5H), 0.91 (t, *J* = 7.2 Hz, 1.7H), 0.84 (t, *J* = 7.2 Hz, 1.3H),; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.48, 158.45, 142.26, 142.23, 139.8, 129.30, 129.26, 126.3, 52.1, 47.2, 45.4, 41.2, 30.7, 28.7, 21.4, 19.9, 19.6, 14.5, 13.7, 13.6, 12.0; HRMS calcd. for $C_{14}H_{22}N_2NaO_2S$ $[M+Na]^+$; 305.1300; found 305.1304.

*4.2.24. (E)-4-methyl-N-(piperidin-1-ylmethylene)benzenesulfonamide* (**3x**):[7a] White solid, mp: 139–141 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 1.67-1.57 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.3, 142.4, 139.8, 129.4, 126.6, 52.0, 44.71, 26.5, 24.9, 24.1, 21.6.

*4.2.25. (E)-4-methyl-N-(1-methylpyrrolidin-2-ylidene)benzenesulfonamide* (**3y**):[7b] White solid, mp: 123–124 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.66 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.86 (s, 3H), 2.81 (d, *J* = 7.6 Hz, 2H), 2.49 (s, 3H), 1.97-1.90 (m, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 169.5, 141.5, 129.2, 125.9, 51.2, 31.5, 30.5, 20.9, 18.5.

*4.2.26. (E/Z)-N-ethyl-N-phenyl-N'-tosylformimidamide* (**3z**):[7a] White solid, mp: 96–97 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.55 (s, 0.2H), 8.35 (s, 0.8H), 7.73 (d, *J* = 8.0 Hz, 1.6H), 7.59(d, *J* = 8.0 Hz, 0.4H), 7.48-7.24 (m, 7H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.37 (s, 2.4H), 2.34(s, 0.6H), 1.04 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 159.8, 158.0, 142.4, 141.5, 139.1, 129.7, 129.5, 129.4, 129.2, 127.8, 127.4, 126.4, 126.2, 125.9, 123.4, 49.6, 43.3, 20.94, 20.91, 14.0, 11.9.

*4.2.27. (E)-N,N-dibutyl-N'-tosylformimidamide* (**3aa**):[7a] viscous oil. $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 3.39 (t, *J* = 7.6 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 1.57-1.49 (m, 4H), 1.33-1.27 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.86(t, *J* = 7.2 Hz, 3H) ; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.8, 142.3, 139.9, 129.3, 126.4, 52.4, 46.1, 30.8, 28.8, 21.6, 20.0, 19.8, 13.8, 13.7.

*4.2.28. (E/Z)- N-isopropyl-N'-tosylacetimidamide* (**3ab**): White solid, mp: 83–84 °C. $^1$H NMR (600 MHz, $CDCl_3$): δ =7.81 (m, 2H), 7.26 (m, 2H), 5.29 (bs, 1H), 4.17- 4.11 (m, 0.7H), 3.74 - 3.68 (m, 0.3H), 2.40 (s, 3H), 2.37 (s, 2H), 2.10 (s, 1H), 1.25 (d, *J* = 6.6 Hz, 2H), 1.15 (d, *J* = 6.6 Hz, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 164.4, 142.8, 142.1, 140.9, 129.4, 129.2, 126.5, 126.4, 46.7, 44.0, 23.5, 22.0, 21.8, 21.65, 21.61. HRMS calcd. for $C_{12}H_{18}N_2NaO_2S$ $[M+Na]^+$; 277.0987; found 277.0985.

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**Appendix A. Supplementary data**

Supplementary data related to this article can be found at t

http:// dx.doi.org/

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