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The synthesis and reaction of *N*-sulfenyl heterocycles: development of effective sulfenylating reagents

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Abstract—Various *N*-sulfenyl heterocycles were synthesized by transamination of sulfenamides using a chlorine gas-free method. The *N*-sulfenyl heterocycles behaved as sulfenylating reagents of anilines; *N*-sulfenylbenzimidazoles were the most effective.

1. Introduction

Compounds containing divalent sulfur–nitrogen bonds, especially sulfenamides, are attractive for their diverse industrial and medicinal applications.[1] Recently, another utility of sulfenamides was reported: some sulfenamides catalyzed oxidation of alcohols (with halogenating reagents as oxidant) to the corresponding carbonyl compounds.[2]

The sulfenamides have generally been synthesized by sulfenylation of amines or amination of thiols.[1,3] To synthesize sulfenylating reagents such as sulfenyl chlorides, chlorine gas was used as the chlorinating reagent. Because the use of chlorine gas sometimes caused undesired complications during laboratory procedures, chlorine gas-free synthetic methods for the sulfenamides have been evaluated.

In previous papers, we reported that both *N*-sulfenyl-1,2-benzisothiazolin-3-ones[4] and *N*-acylsulfenamides[5] were effective sulfenylating reagents for the synthesis of *N*-substituted sulfenamides. These sulfenylating reagents were synthesized by a chlorine gas-free procedure: the transamination of *N*-unsubstituted sulfenamides with 1,2-benzisothiazolin-3-ones[6] or the acylation of *N*-unsubstituted sulfenamides.[7] In the former derivatives, the heterocycles worked as effective leaving groups similar to azoles as leaving groups in *N*-acylazoles in nucleophilic reactions.[8] Although the syntheses of some 2-nitro- and 2,4-dinitrobenzenesulfenyl azoles were reported, sulfenyl chlorides were used in those syntheses.

We also reported that various *N*,*N*-disubstituted sulfenamides were synthesized by the treatment of *N*-unsubstituted sulfenamides with the corresponding amines.[9] In the current study, *N*-containing heterocycles were used as amines, and *N*-sulfenyl heterocycles were synthesized by the transamination of *N*-unsubstituted sulfenamides.

2. Results and discussion

Our first synthesis was an *N*-sulfenylimidazole. Ethyl 2-sulfenamoylbenzoate (**1a**) was treated with imidazole in toluene at 100 °C for 5 h according to the reported transamination procedure.[9] Formation of the desired *N*-[(2-ethoxycarbonylbenzene)sulfenyl]imidazole (**2a**) was confirmed by NMR spectrum after isolation by column chromatography. This product was a viscous liquid that was difficult to isolate in pure form. Furthermore, **2a** decomposed to diethyl 2,2′-dithiodibenzoate during storage. It was reported that sulfenylation of imidazoles with aromatic sulfenyl chlorides produced exclusively diaryl disulfides, and *N*-sulfenylimidazoles were not synthesized by sulfenylation.[10] However, *N*-sulfenylbenzimidazoles were prepared by the reaction of benzimidazole with sulfenyl chlorides in the usual manner.[11] For these reasons, *N*-[(2-ethoxycarbonylbenzene)sulfenyl]benzimidazoles (rather than the obtained *N*-sulfenylimidazole (**2a**)) were the next targets for synthesis.

After the mixture of benzimidazole and ethyl 2-sulfenamoylbenzoate (**1a**) was heated at 100 °C for 5 h, a stable solid

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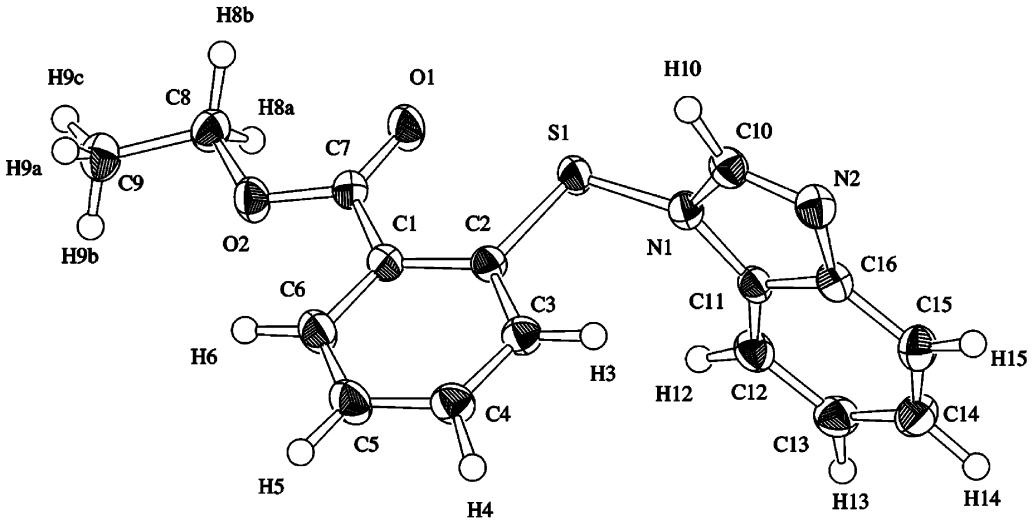


Figure 1. Crystal structure of **2b**.

compound was isolated from the reaction mixture by column chromatography. Spectral data and elemental analysis showed the structure of the product to be consistent with that of *N*-[(2-ethoxycarbonylbenzene)sulfenyl]benzimidazole (**2b**). A single crystal of this compound was obtained, and the structure of the product was confirmed by X-ray crystal analysis (Fig. 1). In the ^{1}H NMR spectrum, the absorption of one aromatic proton was observed in high field, δ 6.10 ppm. X-ray crystal analytical data showed that the 3-H on the benzene ring was located over the benzimidazole ring, causing the high field shift observed in the ^{1}H NMR spectrum.

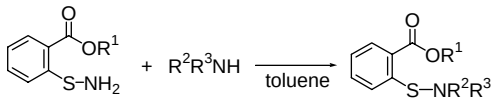
Various *N*-containing heterocycles were treated with the sulfenamides to synthesize *N*-sulfenyl heterocycles; the results are summarized in Table 1. Benzazoles produced high yields of *N*-sulfenyl substituted benzazoles. However, the yield of *N*-sulfenylphthalimide (**2h**) was only 37% (entry 9). The ^{1}H NMR spectra of all the products showed characteristic aromatic proton shift to the high field. In the reaction of methyl 2-sulfenamoylbenzoate (**1b**) at 100 °C, intramolecular cyclization occurred and 1,2-benzisothiazolin-3-one was formed.[12] Therefore, the yields of *N*-sulfenyl heterocycles decreased and *N*-[(2-methoxycarbonylbenzene)-sulfenyl]-1,2-benzisothiazolin-3-one (**2l**) was formed as a by-product with a 17% yield (footnote to entry 3). The yield of **2c** was increased by lowering the reaction temperature to 80 °C (entry 4). 3,5-Dimethylpyrazole produced a stable *N*-sulfenylated product (**2i**) with a high yield (entries 10 and 11), but imidazole produced an unstable product.

To evaluate the utility of sulfenylating reagents in the preparation of *N*-sulfenyl heterocycles, substitution reactions with anilines as nucleophiles were carried out. When *N*-sulfenylbenzimidazole (**2b**) was refluxed with *p*-methylaniline in methanol for 3 h, substitution occurred on the sulfur atom, and *N*-substituted sulfenamide (**4a**) (95% yield) and benzimidazole (96% yield) were isolated. Reactions of the *N*-sulfenyl heterocycles with anilines were carried out under the same conditions; the results are summarized in Table 2. Because *N*-sulfenylimidazole (**2a**) was difficult to handle (see above), the reactions of **2a** were carried out without isolation of **2a** (entry 1). The yields were calculated based on the sulfenamide (**1a**). As reported previously, transamination of sulfenamides (**1**) occurred when they were heated in the presence of anilines.[9] *N*-Substituted sulfenamides could be synthesized in the reaction of **1a** with anilines under methanol refluxing conditions, but the yields were higher when *N*-sulfenyl heterocycles (**2**) were used.

p-Methylaniline produced high yields of **3a** except for the reactions of **2f** and **2h** (entries 6 and 9). It was reported that the reaction of *N*-sulfenylphthalimides with amines gave open-ring products[13] or sulfenamide derivatives.[14] However, the reaction of **2h** with *p*-methylaniline did not proceed and unreacted **2h** was recovered (entry 6). Although *N*-sulfenylphthalimides had been used as sulfenyl reagents, the yield of **2h** and its reactivity with anilines were low. These results indicate that **2h** is not a suitable sulfenylating reagent. The yields of sulfenamide (**3**) decreased when anilines with electron-withdrawing groups were used. It was shown that the rate of these substitution reactions correlated to the nucleophilicity of anilines. *p*-Cyanophenyl substituted sulfenamide (**3d**) was obtained only when using benzimidazole (**2b**), benzotriazole (**2d**), or 3,5-dimethylpyrazole (**2i**) as the starting material. When substituted anilines with electron-withdrawing groups were employed, the solvent reacted with **2** to form a methyl sulfenate derivative (**4**). From these results, it appears that *N*-sulfenylbenzimidazole (**2b**), with its high yield in preparation, stable crystalline structure, and high reactivity with anilines, was the most effective compound for sulfenylation among the compounds prepared.

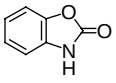
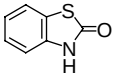
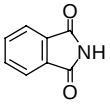
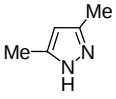
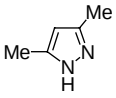
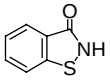
Various *N*-sulfenylbenzimidazoles were synthesized; the results are listed in Table 3. The reaction of (*o*-substituted benzene)sulfenamides with benzimidazole gave *N*-sulfenylbenzimidazoles in good yields. However, (*o*-unsubstituted benzene)sulfenylbenzimidazoles were not synthesized by transamination of sulfenamides. Unsubstituted sulfenamides are usually less stable, and a few could be isolated as stable substances, which are heterocyclic, electron-withdrawing group substituted aromatic, triphenylmethyl,

Table 1. Synthesis of *N*-sulfenyl heterocycles[a]

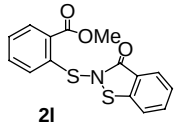


1a: R^1=Et
1b: R^1=Me

2

Entry	**1**	R^2R^3NH	Temperature (°C)	Time (h)	Product	Yield (%)[b]
1	**1a**		100	5	**2a**	51
2	**1a**		100	5	**2b**	92
3[c]	**1b**		100	5	**2c**	54
4	**1b**		80	10	**2c**	78
5	**1a**		100	5	**2d**	95
6	**1a**		100	8	**2e**	78
7	**1a**		100	5	**2f**	73
8	**1a**		100	10	**2g**	77
9	**1a**		100	5	**2h**	37
10	**1a**		100	5	**2i**	90
11	**1b**		80	6	**2j**	50
12[6]	**1a**		100	5	**2k**	66

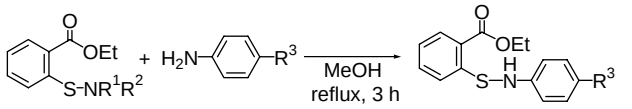
[a] Compound **1**, 2.0 mmol; heterocycles, 2.2 mmol; toluene, 20 mL.
[b] Isolated product.
[c] Compound **2l** was isolated in 17% yield.



2l

and polyhalogenized alkyl sulfenamides as shown in a review.[15] Therefore, it was necessary for transamination reactions under heating conditions to possess such substituents; otherwise unsubstituted sulfenamides, such as benzenesulfenamide or *p*-methylbenzenesulfenamide, decomposed to the corresponding disulfides. Furthermore, *N*-(*p*-ethoxycarbonylbenzene)sulfenyl- and *N*-(*p*-nitrobenzene)sulfenylbenzimidazoles were not prepared. It was reported that nucleophilic attack by the benzimidazole nitrogen of *N*-sulfenylbenzimidazoles occurred on the sulfenyl sulfur atom of another sulfenamide molecule.[11b] It seems that *o*-substituents on the benzenesulfenamide

Table 2. Reaction of *N*-sulfenyl heterocycles with substituted anilines[a]

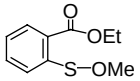


1, **2**

3a: R^3 = Me; **3b**: R^3 = H
3c: R^3 = Cl; **3d**: R^3 = CN

Entry	**1** or **2**	Yield of **3** (%)[b]			
		3a	**3b**	**3c**	**3d**
1[c]	**2a**	86	71	69	5
2	**2b**	95	89	81	43
3	**2d**	98	92	64 (21)	39 (5)
4	**2f**	39			
5	**2g**	80 (11)	48 (17)	7 (38)	0 (32)
6	**2h**	0			
7	**2i**	89	76	35	25
8	**2k**	93	89	12	0 (5)
9	**1a**	69 (12)	26 (12)	8 (11)	0

[a] Compound **1** or **2**, 0.35 mmol; aniline 0.5 mmol; MeOH, 7 mL; reflux; 3 h.
[b] Isolated product. The yields in the parentheses show those of methyl (2-ethoxycarbonylbenzene)sulfenate (**4**).



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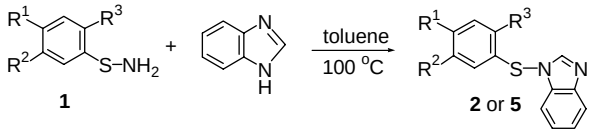
[c] Compound **2a** was not isolated. The yields were calculated based on **1a**.

Table 3. Synthesis of *N*-sulfenylbenzimidazoles[a]



1 **2** or **5**

Entry	Sulfenamide	R^1	R^2	R^3	Time (h)	*N*-Sulfenyl-benzimidazole	Yield (%)[b]
1	**1a**	H	H	CO_2Et	5	**2b**	92
2	**1b**	H	H	CO_2Me	5	**2c**	54
3	**1c**	H	H	CO_2Pr^i	5	**5a**	91
4	**1d**	H	Cl	CO_2Et	10	**5b**	34
5	**1e**	Cl	H	CO_2Et	14	**5c**	63
6	**1f**	MeO	MeO	CO_2Et	11	**5d**	79
7	**1g**	H	H	NO_2	6	**5e**	50

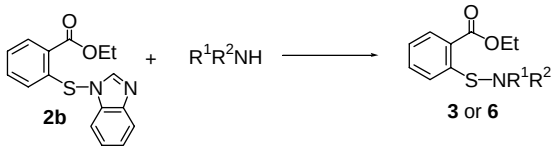
[a] Compound **1**, 2.0 mmol; benzimidazole, 2.0 mmol; toluene, 20 mL.
[b] Isolated product.

hindered the attack by the benzimidazole nitrogen and *N*-sulfenylbenzimidazoles were isolated in good yield. As a result, *o*-substituents on the benzene ring stabilized the unsubstituted sulfenamides during transamination as well as the formed *N*-sulfenylbenzimidazoles. Moreover, *o*-substituents were suitable for the following heterocyclic compound synthesis.[4,12]

Sulfenylation of amines were carried out using *N*-sulfenylbenzimidazole (**2b**); the results are shown in Table 4. First, the reactions of **2b** with primary amines were carried out. The yield of *p*-cyanophenyl substituted sulfenamide (**3d**) increased to 70% by longer reaction time (entry 1) although the yield of **2d** was 43% for 3 h (Table 2, entry 2). Benzylamine reacted with **2b** in good yields under the conditions of methanol reflux for 1.5 h or room temperature for 24 h (entries 2 and 3). Although cyclohexylamine and *t*-butylamine afforded sulfenamides **6b** and **6c** in good yields, respectively, cumylamine gave sulfenamide **6d** in 46% yield but methyl sulfenate **4** was obtained in 28% yield as a by-product under the conditions of methanol reflux for 3 h (entry 6). Therefore, the reaction was carried out in toluene at 100 °C to prevent formation of **4**, and **6d** was obtained in 83% yield (entry 7). The reactions of **2b** with secondary amines afforded *N*,*N*-disubstituted sulfenamides in good yields (entries 7–9). However, it took long reaction time for the reaction with *N*-methylaniline to obtain *N*-methyl-*N*-phenylsulfenamide (**6h**) (entry 11), and diphenylamine did not react with **2b** due to weak nuceophilicity.

Although the sulfenylation of *p*-chloroaniline with *N*-unsubstituted sulfenamide **1a** was very slow, that of benzimidazole produced a high yield of **2b**. Therefore, the synthesis of *N*-chlorophenyl substituted sulfenamide (**3c**) by the sulfenylation with *N*-sulfenyl heterocycles that formed

Table 4. Reaction of *N*-sulfenylbenzimidazole (**2b**) with amines[a]

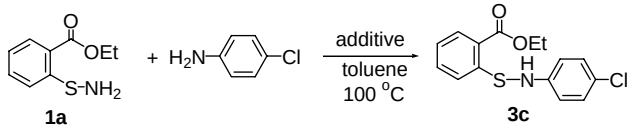


Entry	R^1	R^2	Solvent	Temperature (°C)	Time (h)	Product	Yield (%)[b]
1	*p*-NCC_6H_4	H	MeOH	Reflux	7	**3d**	70
2	$PhCH_2$	H	MeOH	rt	24	**6a**	88
3	$PhCH_2$	H	MeOH	Reflux	1.5	**6a**	86
4	Cyclohexyl	H	MeOH	Reflux	2	**6b**	94
5	*t*-Bu	H	MeOH	70[c]	3	**6c**	79
6	$PhMe_2C$	H	MeOH	Reflux	3	**6d**	46
7	$PhMe_2C$	H	Toluene	100	4.5	**6d**	83
8	Et	Et	MeOH	70[c]	3	**6e**	79
9	$–(CH_2)_4–$		Toluene	100	3	**6f**	86
10	$–(CH_2)_2–O–(CH_2)_2–$		Toluene	100[c]	5	**6g**	95
11	Ph	Me	Toluene	100	20	**6h**	81

[a] *N*-Sulfenylbenzimidazole (**2b**), 0.5 mmol; amine 0.6 mmol; solvent 10 mL.
[b] Isolated product.
[c] In a sealed tube.

in situ was attempted. The results are listed in Table 5. The reaction of **1a** with *p*-chloroaniline produced **3c** with only 6% yield after heating in toluene for 10 h (entry 1). When an equivalent amount of benzimidazole was added to this reaction system, the yield of **3c** increased to 68% (entry 2). *N*-Sulfenylbenzimidazole (**2b**) was formed in situ, and *p*-chloroaniline reacted with **2b** to give the product. Since intermediary *N*-sulfenyl heterocycles were not isolated, imidazole could be used as an additive, and **3c** was obtained with a yield of 75% (entry 5). Addition of 1-methylimidazole also accelerated the formation of **3c** (entry 7). After the reaction of *N*-sulfenyl heterocycles with anilines, the heterocycles were regenerated as leaving groups. Therefore, a catalytic amount of heterocycle was enough to accelerate the reactions (entries 3 and 6).

Table 5. Reaction of sulfenamide (**1a**) with *p*-chloroaniline in the presence of an additive[a]



Entry	Additive	Equiv	Time (h)	Yield (%)[b]
1	—	—	10	6
2	Benzimidazole	1.0	10	68
3	Benzimidazole	0.1	10	19
4	Imidazole	1.0	5	22
5	Imidazole	1.0	12	75
6	Imidazole	0.1	10	52
7	1-Methylimidazole	1.0	10	39

[a] Sulfenamide (**1a**), 0.5 mmol; *p*-chloroaniline 0.6 mmol; toluene 10 mL.
[b] Isolated product.

3. Conclusion

N-Containing heterocycles reacted with 2-sulfenamoylbenzoates when heated to produce high yields of *N*-(2-alkoxycarbonylbenzene)sulfenyl heterocycles. The reactivity of the *N*-sulfenyl heterocycles with substituted anilines was compared; *N*-sulfenylbenzimidazoles produced better yields of *N*-sulfenylanilines than did other heterocycles. Various kinds of *N*-substituted sulfenamides were synthesized by the reaction of *N*-sulfenylbenzimidazoles with amines. In the sulfenylation of anilines with 2-sulfenylbenzoates, the yields of sulfenamides improved by adding heterocycles to the reaction system.

4. Experimental

4.1. General

Melting points were determined on a Mettler FP90 microscopic plate and are uncorrected. ^1H and ^{13}C NMR spectra were obtained with a JEOL LA-500 spectrometer, and chemical shifts (δ) are reported in parts per million relative to internal tetramethylsilane and $CDCl_3$, respectively. IR spectra were recorded on a JASCO FT IR-5300 spectrophotometer. Silica gel column chromatography was carried out on Merck silica gel 60 (0.063–0.200 mm). Elemental analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology. Sulfenamides (**1**) were prepared by the method described in our previous paper.[12]

4.2. General procedure for the synthesis of *N*-sulfenyl heterocycles

To a solution of **1** (2.0 mmol) in toluene (20 mL) was added a heterocycle (2.2 mmol), and the reaction was carried out under the conditions described in Table 1. The solvent was then evaporated, and a crude reaction mixture was chromatographed on silica gel with appropriate eluent.

4.2.1. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]imidazole (2a). Oil; $R_f=0.5$ (CH_2Cl_2/ethyl acetate=1:1); ^1H NMR (500 MHz, $CDCl_3$): δ 1.45 (3H, t, $J=7.0$ Hz), 4.46 (2H, q, $J=7.0$ Hz), 6.11 (1H, d, $J=7.6$ Hz), 7.08 (1H, t, $J=1.2$ Hz), 7.22–7.28 (2H, m), 7.39 (1H, td, $J=7.6$, 1.2 Hz),

7.67 (1H, s), 8.07 (1H, dd, J=7.6, 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 62.0, 121.6, 123.6, 125.0, 125.4, 130.6, 131.1, 133.9, 143.2, 145.5, 167.1; IR (KBr): ν_{max} 2983, 1688, 1463, 1280, 1156, 1057, 743 cm^{-1}; HRMS: Calcd for $C_{12}H_{12}N_2O_2S$: 248.0619. Found: 248.0597.

4.2.2. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]benzimidazole (2b). Mp 136.8–138.0 °C (from ethyl acetate–hexane); R_f=0.3 (CH_2Cl_2/ethyl acetate=20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.48 (3H, t, J=7.3 Hz), 4.50 (2H, q, J=7.3 Hz), 6.10 (1H, d, J=7.9 Hz), 7.20–7.27 (2H, m), 7.34 (1H, t, J=7.6 Hz), 7.37 (1H, t, J=7.6 Hz), 7.51 (1H, d, J=7.9 Hz), 7.90 (1H, d, J=7.6 Hz), 8.03 (1H, s), 8.11 (1H, d, J=7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 62.1, 111.0, 120.8, 121.8, 123.5, 124.2, 124.5, 125.5, 131.0, 133.8, 136.2, 143.9, 144.3, 148.3, 167.2; IR (KBr): ν_{max} 1692, 1146, 748 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73; N, 9.39. Found: C, 64.55; H, 4.67; N, 9.15.

4.2.3. *N*-[(2-Methoxycarbonylbenzene)sulfenyl]benzimidazole (2c). Mp 167.2–169.2 °C (from ethyl acetate–hexane); R_f=0.5 (CH_2Cl_2/ethyl acetate=10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.04 (3H, s), 6.11 (1H, dd, J=8.2, 1.2 Hz), 7.21–7.29 (2H, m), 7.33–7.40 (2H, m), 7.51 (1H, dd, J=7.2, 0.9 Hz), 7.90 (1H, dt, J=7.9, 0.9 Hz), 8.04 (1H, s), 8.09 (1H, dd, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.9, 111.0, 120.8, 121.9, 123.5, 123.8, 124.5, 125.5, 131.0, 133.9, 136.2, 143.9, 144.3, 148.3, 167.6; IR (KBr): ν_{max} 1698, 1433, 1300, 1142, 748 cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85. Found: C, 63.26; H, 4.15; N, 9.66.

4.2.4. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]benzotriazole (2d). Mp 152.0–154.0 °C (from ethyl acetate–hexane); R_f=0.5 (CH_2Cl_2/ethyl acetate=100:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.49 (3H, t, J=7.3 Hz), 4.50 (2H, q, J=7.3 Hz), 5.85–5.87 (1H, m), 7.21–7.26 (2H, m), 7.47 (1H, ddd, J=8.2, 7.0, 0.9 Hz), 7.55 (1H, ddd, J=7.9, 7.0, 0.9 Hz), 7.63 (1H, dt, J=8.2, 0.9 Hz), 8.09–8.11 (1H, m), 8.19 (1H, dt, J=8.2, 0.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 62.3, 110.5, 120.5, 122.1, 124.2, 124.8, 125.7, 128.9, 130.8, 133.8, 137.2, 143.6, 145.9, 167.4; IR (KBr): ν_{max} 1687, 1300, 1007, 748 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_3O_2S$: C, 60.18; H, 4.38; N, 14.04. Found: C, 60.18; H, 4.28; N, 13.82.

4.2.5. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]benzoxazol-2-one (2e). Mp 166.5–168.3 °C (from ethyl acetate–hexane); R_f=0.5 (CH_2Cl_2/ethyl acetate=100:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (3H, t, J=7.2 Hz), 4.47 (2H, q, J=7.2 Hz), 6.82 (1H, dd, J=8.2, 0.6 Hz), 7.17–7.25 (5H, m), 7.40–7.43 (1H, m), 8.10 (1H, dd, J=7.8, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 62.1, 110.4, 110.5, 121.4, 123.9, 124.4, 124.8, 125.5, 131.2, 132.3, 133.6, 141.8, 143.2, 155.2, 167.1; IR (KBr): ν_{max} 1793, 1684, 1474, 1274, 750 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_4S$: C, 60.94, H, 4.16, N, 4.44. Found: C, 60.89; H, 4.13; N, 4.32.

4.2.6. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]benzothiazol-2-one (2f). Mp 138.8–139.5 °C (from ethyl acetate–hexane); R_f=0.7 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (3H, t, J=7.0 Hz), 4.47 (2H, q, J=7.0 Hz), 6.70 (1H, dd, J=8.2, 0.6 Hz), 7.21–7.29 (3H, m), 7.35–7.40 (2H, m), 7.48 (1H, dd, J=7.6, 1.5 Hz), 8.10 (1H, dd, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 62.1, 113.3, 121.7, 122.8, 123.0, 124.7, 125.0, 125.4, 126.9, 131.3, 133.7, 137.9, 141.9, 167.2, 171.4; IR (KBr): ν_{max} 1701, 1458, 1281, 1138, 747 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_3S_2$: C, 57.99; H, 3.95; N, 4.23. Found: C, 57.99; H, 3.85; N, 4.15.

4.2.7. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]-2,1-benzisothiazoline-3-one (2g). Mp 160.8–161.8 °C (from ethyl acetate–hexane); R_f=0.6 (CH_2Cl_2/ethyl acetate=100:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (3H, t, J=7.3 Hz), 4.46 (2H, q, J=7.3 Hz), 6.84 (1H, dd, J=8.2, 0.6 Hz), 7.16 (1H, ddd, J=7.9, 6.7, 1.2 Hz), 7.26 (1H, ddd, J=7.9, 7.3, 0.6 Hz), 7.42 (1H, ddd, J=8.2, 7.3, 1.2 Hz), 7.54 (1H, dd, J=6.7, 1.5 Hz), 7.57 (1H, ddd, J=7.9, 7.3, 1.5 Hz), 7.89 (1H, dd, J=7.3, 1.2 Hz), 8.10 (1H, dd, J=7.9, 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 62.0, 113.6, 121.5, 121.9, 122.9, 123.8, 124.6, 125.5, 131.2, 133.6, 134.6, 144.6, 155.3, 167.0, 190.0; IR (KBr): ν_{max} 1682, 1601, 1468, 1312, 1154, 941, 897, 743 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_3S_2$: C, 57.99; H, 3.95; N, 4.23. Found: C, 58.32; H, 3.78; N, 4.11.

4.2.8. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]phthalimide (2h). Mp 228.0–229.0 °C (from ethyl acetate); R_f=0.6 (CH_2Cl_2/ethyl acetate=10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.44 (3H, t, J=7.3 Hz), 4.46 (2H, q, J=7.3 Hz), 6.87 (1H, dd, J=8.2, 0.9 Hz), 7.22 (1H, td, J=7.9, 1.2 Hz), 7.39 (1H, ddd, J=8.2, 7.3, 1.5 Hz), 7.85–7.86 (2H, m), 8.02–8.02 (2H, m), 8.08 (1H, dd, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 61.9, 121.5, 124.2, 125.1, 125.2, 131.2, 132.2, 133.3, 134.9, 142.6, 166.9, 168.1; IR (KBr): ν_{max} 1740, 1688, 1273, 1046, 748, 711 cm^{-1}. Anal. Calcd for $C_{17}H_{13}NO_4S$: C, 62.37; H, 4.00; N, 4.28. Found: C, 62.41; H, 3.84; N, 4.28.

4.2.9. *N*-[(2-Ethoxycarbonylbenzene)sulfenyl]-3,5-dimethylpyrazole (2i). Mp 95.2–96.2 °C (from hexane); R_f=0.6 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (3H, t, J=7.2 Hz), 2.26 (3H, s), 2.30 (3H, s), 4.44 (2H, q, J=7.2 Hz), 6.04 (1H, dd, J=8.2, 0.9 Hz), 6.06 (1H, s), 7.19 (1H, td, J=7.9, 0.9 Hz), 7.36 (1H, ddd, J=8.2, 7.3, 1.4 Hz), 8.04 (1H, dd, J=7.9, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.7, 14.0, 14.3, 61.8, 107.5, 122.4, 123.9, 125.0, 130.7, 133.6, 146.4, 147.6, 152.4, 166.8; IR (KBr): ν_{max} 1686, 1562, 1462, 1294, 743 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.95; H, 5.79; 10.10.

4.2.10. *N*-[(2-Methoxycarbonylbenzene)sulfenyl]-3,5-dimethylpyrazole (2j). Mp 91.8–93.2 °C (from hexane); R_f=0.5 (CH_2Cl_2/ethyl acetate=10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (3H, s), 2.30 (3H, s), 3.98 (3H, s), 6.04 (1H, dd, J=8.2, 0.9 Hz), 6.07 (1H, s), 7.19 (1H, ddd, J=7.8, 7.3, 0.9 Hz), 7.37 (1H, ddd, J=8.2, 7.3, 1.5 Hz), 8.02 (1H, dd, J=7.8, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.7, 14.0, 52.6, 103.2, 107.6, 122.4, 123.5, 125.0, 130.7, 133.7, 146.5, 147.5, 152.4, 161.1, 167.2; IR (KBr): ν_{max} 1695, 1564, 1462, 1437, 1278, 790, 752 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.61; H, 5.30; N, 10.34.

4.2.11. *N*-[(2-Methoxycarbonylbenzene)sulfenyl]-1,2-benzisothiazolin-3-one (2l).[12] Mp 187.5–189 °C (from benzene–hexane); R_f=0.5 (CH_2Cl_2/ethyl acetate=20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.98 (3H, s), 6.83 (1H, dd, J=8.2, 0.6 Hz), 7.24 (1H, td, J=7.5, 0.9 Hz), 7.40–7.47 (2H, m), 7.57 (1H, d, J=7.9 Hz), 7.71 (1H, ddd, J=8.2, 7.0, 0.9 Hz), 8.06 (1H, dd, J=7.9, 1.4 Hz), 8.13 (1H, d, J=7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.7, 120.6, 122.0, 122.8, 124.4, 125.3, 125.7, 127.8, 131.0, 133.1, 133.6, 142.9, 143.4, 167.1, 167.4; IR (KBr): ν_{max} 1680, 1317, 1281, 1107, 733 cm^{-1}.

4.3. X-ray crystallographic analysis of 2b

X-ray crystallographic analysis was carried out on a Rigaku AFC7R diffractometer using a rotating anode with graphite monochromated Mo Kα radiation (λ=0.7107 Å). Crystal data for **2b**: $C_{16}H_{14}N_2O_2S$, M=298.36, monoclinic, space group $P2_1/c$ (No. 14), a=7.6501(18), b=8.0237(13), c=23.6292(10) Å, β=92.058(9)°, V=1449.5(4) Å^3, T=173(2) K, Z=4, D_{calcd}=1.367 g cm^{-3}, μ=0.229 mm^{-1}; goodness of fit=1.034; $R1$ [$I>2\sigma(I)$]=0.0335, $wR2$=0.0777 (all data).

Selected bond distances (Å) and angles (°) are shown as follows: S(1)–N(1) 1.7015(12), S(1)–C(2) 1.7863(14); O(1)–C(7) 1.2119(18), C(1)–C(7) 1.475(2); N(1)–S(1)–C(2) 100.35(6), S(1)–N(1)–C(11) 127.62(10), C(2)–C(1)–C(7) 119.38(12), S(1)–C(2)–C(3) 122.04(11), O(1)–C(7)–C(1) 123.18(13). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 285609. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.4. General procedure for reaction of 2 with anilines

To a solution of **2** (0.35 mmol) in methanol (7 mL) was added an aniline (0.5 mmol). After 3 h of refluxing, the solvent was evaporated and a crude reaction mixture was chromatographed on silica gel with dichloromethane or dichloromethane–hexane (2/1). The structures of products **3a** and **3b** were identical to those of the compounds that we previously reported.[4,9]

4.4.1. Ethyl *N*-(*p*-chlorophenyl)-2-sulfenamoylbenzoate (3c). Mp 110.0–110.7 °C (from ethyl acetate–hexane); R_f=0.5 (CH_2Cl_2/hexane=2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (3H, t, J=7.3 Hz), 4.42 (2H, q, J=7.0 Hz), 5.09 (1H, s), 6.90–6.93 (2H, m), 7.14–7.20 (3H, m), 7.42–7.43 (2H, m), 8.07 (1H, dt, J=7.6, 0.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 61.5, 115.7, 122.3, 124.4, 124.6, 125.1, 129.2, 131.3, 132.9, 145.0, 147.4, 166.7; IR (KBr): ν_{max} 3355, 1684, 1493, 1271, 1144, 1101, 820, 745 cm^{-1}. Anal. Calcd for $C_{15}H_{14}ClNO_2S$: C, 58.53; H, 4.58; N, 4.55. Found: C, 58.51; H, 4.52; N, 4.46.

4.4.2. Ethyl *N*-(*p*-cyanophenyl)-2-sulfenamoylbenzoate (3d). Mp 148.0–149.5 °C (from ethyl acetate–hexane); R_f=0.5 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.44 (3H, t, J=7.3 Hz), 4.43 (2H, q, J=7.3 Hz), 5.49 (1H, s), 7.03 (2H, dd, J=7.0, 2.1 Hz), 7.22 (1H, td, J=7.5, 1.2 Hz), 7.34 (1H, d, J=7.5 Hz), 7.44 (1H, td, J=7.5, 1.5 Hz), 7.49 (2H, dd, J=7.0, 2.1 Hz), 8.09 (1H, td, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 61.6, 103.0, 114.9, 119.6, 122.0, 124.7, 124.8, 131.4, 133.1, 133.8, 146.1, 150.6, 166.8; IR (KBr): ν_{max} 3322, 2220, 1688, 1603, 1507, 1462, 1277, 1146, 895, 831, 745 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73; N, 9.39. Found: C, 64.23; H, 4.65; N, 9.39.

4.4.3. Methyl (2-ethoxycarbonylbenzene)sulfenate (4). Bp 150 °C (13.3 Pa); R_f=0.4 (CH_2Cl_2/hexane=1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (3H, t, J=7.2 Hz), 3.79 (3H, s), 4.39 (2H, q, J=7.2 Hz), 7.17–7.20 (1H, m), 7.59–7.61 (2H, m), 8.02 (1H, d, J=7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 61.6, 64.2, 119.9, 121.8, 123.6, 130.5, 133.1, 149.2, 167.0; IR (neat): ν_{max} 2981, 1685, 1460, 1280, 989, 743, 692 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70. Found: C, 56.57; H, 5.71.

4.5. General procedure for the synthesis of *N*-sulfenylbenzimidazoles

To a solution of a sulfenamide (2.0 mmol) in toluene (20 mL) was added benzimidazole (2.2 mmol), and the reaction was carried out under the conditions described in Table 3. The solvent was then evaporated, and a crude reaction mixture was chromatographed on silica gel with appropriate eluent.

4.5.1. *N*-[(2-Isopropoxycarbonylbenzene)sulfenyl]benzimidazole (5a). Mp 113.5–115.0 °C (from hexane); R_f=0.5 (ethyl acetate/hexane=1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (6H, d, J=6.1 Hz), 5.36 (1H, hept, J=6.1 Hz), 6.09 (1H, dd, J=8.2, 0.9 Hz), 7.20–7.27 (2H, m), 7.33–7.39 (2H, m), 7.52 (1H, dd, J=7.8, 1.5 Hz), 7.90 (1H, dd, J=7.1, 1.5 Hz), 8.03 (1H, s), 8.09 (1H, dd, J=7.6, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.0, 70.0, 111.0, 120.8, 121.8, 123.5, 124.4, 124.6, 125.4, 131.0, 133.7, 136.2, 144.0, 144.1, 148.3, 166.8; IR (KBr): ν_{max} 1696, 1296, 1177, 1101, 741 cm^{-1}. Anal. Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16; N, 8.97. Found: C, 65.22; H, 5.07; N, 8.99.

4.5.2. *N*-[(4-Chloro-2-ethoxycarbonylbenzene)sulfenyl]-benzimidazole (5b). Mp 145.7–146.7 °C (from ethyl acetate–hexane); R_f=0.4 (CH_2Cl_2/acetone=20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47 (3H, t, J=7.0 Hz), 4.49 (2H, q, J=7.0 Hz), 6.12 (1H, d, J=1.8 Hz), 7.17 (1H, dd, J=8.5, 1.8 Hz), 7.38 (2H, m), 7.51 (1H, dd, J=8.8, 1.5 Hz), 7.91 (1H, dd, J=8.5, 1.5 Hz), 8.02 (1H, d, J=8.2 Hz), 8.03 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 62.4, 110.8, 121.0, 121.8, 122.6, 123.7, 124.7, 126.0, 132.1, 135.9, 140.9, 143.9, 146.3, 147.9, 166.5; IR (KBr): ν_{max} 1696, 1580, 1443, 1273, 1098, 747 cm^{-1}. Anal. Calcd for $C_{16}H_{13}ClN_2O_2S$: C, 57.74; H, 3.94; N, 8.42. Found: C, 57.82; H, 3.71; N, 8.31.

4.5.3. *N*-[(5-Chloro-2-ethoxycarbonylbenzene)sulfenyl]-benzimidazole (5c). Mp 128.4–129.4 °C (from ethyl acetate–hexane); R_f=0.4 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.48 (3H, t, J=7.0 Hz), 4.50 (2H, q, J=7.0 Hz), 6.02 (1H, d, J=8.8 Hz), 7.21 (1H, dd, J=8.8, 2.4 Hz), 7.33–7.40 (2H, m), 7.48 (1H, dd, J=7.6, 1.5 Hz), 7.90 (1H, dd, J=7.9, 1.5 Hz), 8.02 (1H, s), 8.07 (1H, d, J=2.4 Hz);

^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 62.6, 110.9, 120.9, 123.3, 123.7, 124.6, 125.3, 130.7, 131.7, 133.7, 136.0, 142.7, 143.9, 148.1, 166.2; IR (KBr): ν_{max} 1694, 1443, 1310, 1250, 1169, 1128, 1040, 737 cm^{-1}. Anal. Calcd for $C_{16}H_{13}ClN_2O_2S$: C, 57.74; H, 3.94; N, 8.42. Found: C, 57.90; H, 3.85; N, 8.25.

4.5.4. *N*-[(4,5-Dimethoxy-2-ethoxycarbonylbenzene)-sulfenyl]benzimidazole (5d). Mp 161.7–163.7 °C (from ethyl acetate–hexane); R_f=0.4 (CH_2Cl_2/acetone/methanol=100:10:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.48 (3H, t, J=7.0 Hz), 3.20 (3H, s), 3.89 (3H, s), 4.48 (2H, q, J=7.0 Hz), 5.31 (1H, s), 7.33–7.37 (2H, m), 7.50 (1H, s), 7.53 (1H, d, J=5.2 Hz), 7.88 (1H, d, J=5.2 Hz), 8.07 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.5, 55.5, 56.2, 61.9, 104.1, 111.2, 112.6, 115.9, 120.7, 123.5, 124.5, 136.2, 137.8, 143.8, 148.6, 153.9, 166.9; IR (KBr): ν_{max} 1672, 1508, 1476, 1443, 1292, 1211, 1179, 1020, 737 cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O_4S$: C, 60.32; H, 5.06; N, 7.82. Found: C, 60.36; H, 4.95; N, 7.66.

4.5.5. *N*-[(2-Nitrobenzene)sulfenyl]benzimidazole (5e). Mp 167.0–168.8 °C (from ethyl acetate) (lit.,[16] 164.5–165 °C); R_f=0.2 (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.23 (1H, dd, J=8.2, 1.2 Hz), 7.35–7.44 (4H, m), 7.50 (1H, dd, J=7.2, 1.2 Hz), 7.92 (1H, dd, J=7.2, 1.2 Hz), 8.06 (1H, s), 8.39 (1H, dd, J=8.1, 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 110.5, 120.8, 123.1, 123.7, 124.6, 125.6, 126.4, 135.0, 135.4, 139.7, 142.1, 143.6, 147.4; IR (KBr): ν_{max} 3064, 1590, 1566, 1514, 1447, 1332, 1310, 1260, 1173, 1146, 738 cm^{-1}.

4.6. General procedure for reaction of 2a with amines

To a solution of **2a** (0.5 mmol) in methanol (10 mL) was added an aniline (0.6 mmol). The reaction was carried out under the conditions described in Table 4. The solvent was then evaporated, and a crude reaction mixture was chromatographed on silica gel with appropriate eluent. The structures of products **6a**, **6c**, **6d**, **6e**, **6f**, and **6g** were identical to those of the compounds that we previously reported.[9]

4.6.1. Ethyl *N*-cyclohexyl-2-sulfenamoylbenzoate (6b). Mp 69.0–70.7 °C (from hexane); R_f=0.4 (CH_2Cl_2/hexane=2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14–1.26 (6H, m), 1.39 (3H, t, J=7.2 Hz), 1.71–1.74 (2H, m), 2.04–2.07 (2H, m), 2.53 (1H, br s), 2.71 (1H, br s), 4.37 (2H, q, J=7.2 Hz), 7.12 (1H, ddd, J=7.8, 7.0, 1.2 Hz), 7.50 (1H, ddd, J=8.2, 7.0, 1.4 Hz), 7.94 (1H, dd, J=8.2, 0.6 Hz), 8.00 (1H, dd, J=7.8, 1.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 24.9, 25.9, 34.0, 59.1, 61.0, 122.9, 123.3, 124.0, 131.1, 132.2, 150.0, 166.5; IR (KBr): ν_{max} 3301, 2927, 1685, 1264, 1145, 1051, 738 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.48; H, 7.55; N, 4.90.

4.6.2. Ethyl *N*-methyl-*N*-phenyl-2-sulfenamoylbenzoate (6h). Mp 78.2–79.7 °C (from hexane); R_f=0.5 (CH_2Cl_2/hexane=2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.44 (3H, t, J=7.3 Hz), 3.47 (3H, s), 4.43 (2H, q, J=7.3 Hz), 5.49 (1H, s), 7.03 (2H, dd, J=7.0, 2.1 Hz), 7.22 (1H, td, J=7.5, 1.2 Hz), 7.34 (1H, d, J=7.5 Hz), 7.44 (1H, td, J=7.5, 1.5 Hz), 7.49 (2H, dd, J=7.0, 2.1 Hz), 8.09 (1H, td, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 43.3, 61.4, 114.6, 119.3, 122.3, 124.2, 124.4, 129.1, 131.5, 132.9, 147.3, 149.1, 166.7; IR (KBr): ν_{max} 1696, 1599, 1295, 1460, 1368, 1271, 1148, 1086, 862, 748, 691 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.88; H, 5.97; N, 4.87.

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