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Reactions of *N*-sulfenyl-1,2-benzisothiazolin-3-ones with nucleophiles

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Abstract—Reactions of *N*-[2-(alkoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-ones (**1**) with various nucleophiles were examined. Anions of active methylene compounds attacked the sulfur atoms of the sulfenyl moieties of **1** to afford sulfide compounds, while thiols attacked the sulfur atoms of the benzisothiazolinone moieties of **1** to afford ring-opened products. Grignard reagents attacked both the above sulfur atoms to give ring-opened products along with sulfide compounds.

1. Introduction

The transformation of organosulfur compounds to other sulfur-containing compounds is of importance in various applications.[1] Several organosulfur compounds have been used as intermediates for synthesis of other sulfur-containing compounds.[1b,2] Among them, sulfenamides are useful sulfenylating reagents, and they react with various nucleophiles such as amines,[2–4] active methylene compounds,[4–6] and thiols[2,4,7,8] to afford corresponding sulfenylated products in high yields. In particular, the introduction of heterocyclic leaving groups into sulfenamides leads to a remarkable increase in the reactivity of sulfenamides in substitution reactions.[3,4,6,8] Exceptional examples are reactions of *N*-sulfenylated phthalimides and succinimides with primary amines to give ring-opened products.[9] In a previous paper,[10] we reported that the substitution reaction of *N*-[2-(alkoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-ones (**1**) with amines efficiently afforded *N*-substituted 2-sulfenamoylbenzoates. In these reactions, nucleophiles selectively attacked the sulfur atom of the sulfenyl moieties of **1**, and the 1,2-benzisothiazolin-3-one group behaved as an excellent leaving group. During our ongoing investigation of the substitution reactions of **1** with other nucleophiles, we found that there are two reaction sites on **1**: anions of active methylene compounds attacked the sulfur atoms of the sulfenyl moieties of **1** to afford sulfide compounds, while thiols attacked the sulfur atoms of the benzisothiazolinone moieties of **1** to give ring-opened products. Grignard reagents attacked both the above sulfur atoms to produce the mixture of sulfides and ring-opened products.

2. Results and discussion

2.1. Substitution reaction of 1a with active methylene compounds

Initially, we examined the influence of the bases triethylamine, pyridine, and sodium hydride in a model reaction of *N*-[2-(methoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-one (**1a**) with diethyl malonate in THF. When the reaction was carried out in the presence of triethylamine or pyridine, none of the desired product, diethyl 2-[2-(methoxycarbonyl)benzenesulfenyl]malonate (**2a**), was obtained, even when the reaction mixture was refluxed for several hours, and only starting materials were recovered. However, **2a** was obtained in 78% yield when the reaction was carried out in the presence of sodium hydride (1.5 equiv) at room temperature for 1 h (Table 1, entry 1). We next examined the substitution reaction of various active methylene compounds with **1a** under the same reaction conditions (Table 1, entries 2–6). Reactions of **1a**

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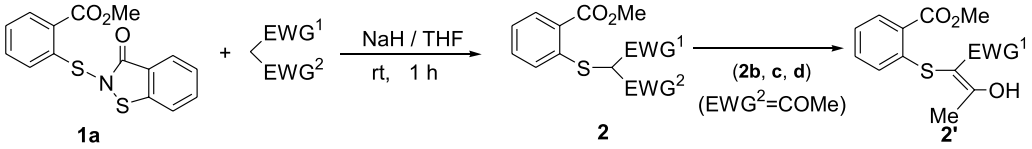
Table 1. Substitution reaction of *N*-[2-(methoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-one (**1a**) with active methylene compounds



Entry	EWG^1	EWG^2	Yield (%) of **2**[a]	
1	CO_2Et	CO_2Et	**2a**	78
2	CO_2Et	COMe	**2b**	88
3	COPh	COMe	**2c**	73
4	COMe	COMe	**2d**	81
5	CN	CO_2Et	**2e**	74
6	CN	SO_2Ph	**2f**	91

[a] Isolated product.

with active methylene compounds having an acetyl group proceeded smoothly: ethyl acetoacetate, 1-benzoylacetone, and acetylacetone provided ethyl 2-[2-(methoxycarbonyl)-benzenesulfenyl]-2-acetylacetate (**2b**), 1-phenyl-2-[2-(methoxycarbonyl)benzenesulfenyl]butan-1,3-dione (**2c**), and 3-[2-(methoxycarbonyl)benzenesulfenyl]pentan-2,4-dione (**2d**) in good yields (88, 73, and 81%, respectively; entries 2–4). The NMR spectra of **2b**, **2c**, and **2d** showed that they existed as the enol isomers **2′** in $CDCl_3$. For example, the ^1H NMR spectrum of **2d** in $CDCl_3$ displayed a singlet peak at low field (δ_H 17.4), which was assigned to the O–*H* of the enol isomer of **2d**; the ^{13}C NMR signal of the S–*C* of **2d** shifted downfield (δ_C 101.5), which indicated that the carbon transformed to sp^2 carbon. This observation is in agreement with the isomerization found for α-sulfenyl-β-dicarbonyl compounds, which exist in the enol form in $CDCl_3$.[11] Reactions of **1a** with ethyl cyanoacetate and (phenylsulfonyl)acetonitrile proceeded smoothly and provided ethyl 2-[2-(methoxycarbonyl)benzenesulfenyl]-2-cyanoacetate (**2e**) and 2-[2-(methoxycarbonyl)benzenesulfenyl]-2-(phenylsulfonyl)acetonitrile (**2f**) in good yields (74 and 91%, respectively; entries 5 and 6).

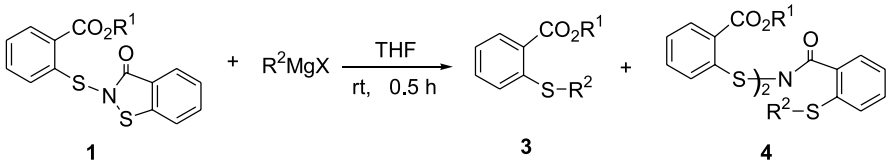
2.2. Substitution reactions of 1 with Grignard reagents

When the reaction of *N*-[2-(ethoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-one (**1b**) with a small excess of methylmagnesium bromide was carried out in THF at room temperature for 0.5 h, the desired product, sulfide derivative **3a**, was obtained in only 13% yield. Interestingly, an unexpected product, *N*,*N*-disulfenyl-2-(methylthio)benzamide derivative **4a**, was isolated in 45% yield as a major product (Table 2, entry 1). The structure of **4a** was determined by IR and NMR spectroscopy and elemental analysis. No N–H absorption was observed in the IR spectrum. The resonances for CH_2 and CH_3 of the OCH_2CH_3 group were observed at δ_H 4.35 and 1.34, respectively, and a single resonance for the S–CH_3 group was observed at δ_H 2.55 in the ^1H NMR spectrum. Two resonances were observed in the O=*C* region at δ_C 175.8 and 166.6 in the ^{13}C NMR spectrum and were assigned to the carbonyl groups of the amide and ester moieties, respectively. The similar ring-opened products, **4b** (41%, entry 2) and **4c** (47%, entry 3), were also obtained as major products when **1b** was treated with benzylmagnesium chloride or phenylmagnesium bromide, respectively. Reaction of **1a** with phenylmagnesium bromide gave **4d** in 32% yield along with **3d** in 40% yield (entry 4). To further explore the structure of **4**, a single-crystal X-ray diffraction study of **4b** was performed. The molecular structure of **4b** is shown in Figure 1, and the structure was consistent with that of *N*,*N*-disulfenyl-2-(methylthio)benzamide.

A plausible mechanism for the formation of **4** is shown in Scheme 1. In this mechanism, the Grignard reagent attacks the sulfur atom of the 1,2-benzisothiazolin-3-one moiety of **1** to generate an amide anion. The amide anion then attacks the sulfur atom of the sulfenamide moiety of another molecule of **1** to form **4** along with 1,2-benzisothiazolin-3-one as a leaving group.

The foregoing results clearly showed that reactions of

Table 2. Reaction of *N*-sulfenyl-1,2-benzisothiazolin-3-ones **1** with Grignard reagents



Entry	**1**	R^1	R^2	X	Product			
					3	Yield[a] (%)	**4**	Yield[a] (%)
1	**1b**	Et	Me	Br	**3a**	13	**4a**	45
2	**1b**	Et	$PhCH_2$	Cl	**3b**	30	**4b**	41
3	**1b**	Et	Ph	Br	**3c**	26	**4c**	47
4	**1a**	Me	Ph	Br	**3d**	40	**4d**	32

[a] Isolated product.

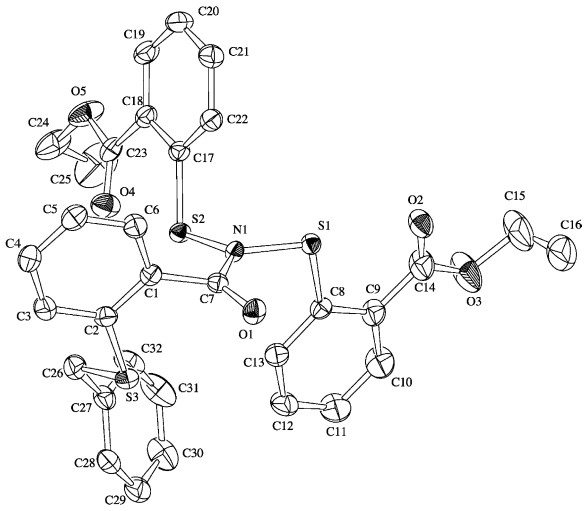
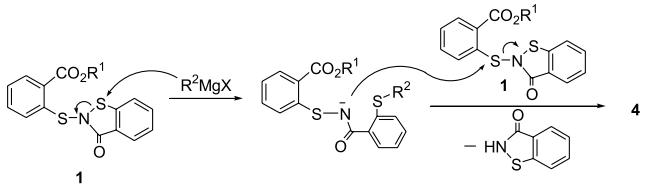


Figure 1. Crystal structure of **4b**.



Scheme 1. A plausible mechanism for the formation of **4**.

N-sulfenylated 1,2-benzisothiazolin-3-ones with Grignard reagents occurred on the sulfur atom in the ring. However, in 1952 it was reported that Grignard reagents added to the carbonyl group of *N*-aryl-substituted 1,2-benzisothiazolin-3-ones to afford hydroxyl compounds **6′**.[12] To verify our results, we re-examined the reactions of *N*-aryl- and *N*-aralkyl-substituted 1,2-benzisothiazolin-3-ones with Grignard reagents (Table 3). The reaction of *N*-phenyl-1,2-benzisothiazolin-3-one (**5a**) with 1.4 equiv of methylmagnesium bromide did not give hydroxyl compound **6′a**, but afforded a ring-opened product, *N*-phenyl-2-(methylthio)benzamide (**6a**), with the same melting point as reported in the literature[12] (entry 1). The structure of **6a** was established by IR and NMR spectroscopy. A sharp absorption at $\nu = 3300\ \mathrm{cm}^{-1}$ in the IR spectrum was assigned to the N–H bond. The resonance for O=*C* of the amide group was observed at δ_C 166.0 in the ^{13}C NMR spectrum. The agreement between the melting point of **6a** and that reported for *N*-phenyl-2-(methylthio)benzamide obtained by the reaction of 2-(methylthio)benzoyl chloride with aniline[13] confirmed the structure. Reactions of **5a–c** with phenylmagnesium bromide or methylmagnesium bromide also provided ring-opened products, **6b–e**, in moderate to high yields (entries 2–5).

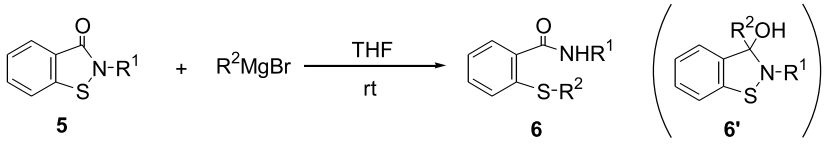
2.3. Substitution reaction of 1 with thiols

Reaction of **1a** with 1 equiv of 1-dodecanethiol in methanol at room temperature for 0.5 h gave a ring-opened product, *N*-[2-(methoxycarbonyl)benzenesulfenyl]-2-(dodecyldithio)benzamide (**7a**), in 92% yield (Table 4, entry 1). Ring-opened products, *N*-[2-(ethoxycarbonyl)benzenesulfenyl]-2-(dodecyldithio)benzamide (**7b**) and *N*-[2-(ethoxycarbonyl)benzenesulfenyl]-2-(octyldithio)benzamide (**7c**), were also obtained in excellent yields from the reactions of **1b** with 1-dodecanethiol and 1-octanethiol under the same reaction conditions (Table 4, entries 2 and 3). When **7a** was treated with 1 equiv of 1-dodecanethiol in methanol at 40 °C for 1 h, two kinds of unsymmetrical disulfides, methyl 2-(dodecyldithio)benzoate (**8**) and 2-(dodecyldithio)benzamide (**9**), were obtained in 70 and 77% yields, respectively (Scheme 2, Eq. (1)). The foregoing results suggested that thiols could react with 1,2-benzisothiazolin-3-one (**10**) and *N*-alkyl-substituted derivatives to afford ring-opened products.[14] Indeed, when **10** and **11** were treated with 1-dodecanethiol in methanol at room temperature for 0.5 h, respectively, the corresponding products **9** and **12** were obtained in good yields (98 and 76%, respectively; Scheme 2, Eq. (2)).

3. Conclusion

Reactions of *N*-[2-(alkoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-ones (**1**) with various nucleophiles were examined. Anions of active methylene compounds, like amines,[10] attacked the sulfur atoms of the sulfenyl moieties of **1** to afford sulfide compounds. However, in the case of thiols, reaction occurred on the benzisothiazolinone ring moieties of **1** to give ring-opened products. Grignard reagents attacked both the above sulfur atoms to produce the mixtures of sulfides and ring-opened products. These results

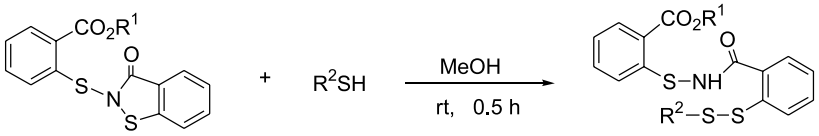
Table 3. Reaction of 1,2-benzisothiazolin-3-ones **5** with Grignard reagents



Entry	5	R^1	R^2	Time (h)	6	Yield[a] (%)	Mp (°C)		
							Observed	6, reported[b]	6′, reported[c]
1	**5a**	Ph	Me	3	**6a**	41	146.7–147.5	148–149	150
2	**5a**	Ph	Ph	1	**6b**	79	118.7–119.0	—	170
3	**5b**	*p*-MeC_6H_4	Me	3	**6c**	67	144.1–145.5	145–146	—
4	**5c**	$PhCH_2CH_2$	Me	1.5	**6d**	55	118.1–118.6	—	—

[a] Isolated product.
[b] Uchida, Y.; Kozuka, S. *Bull. Chem. Soc. Jpn* **1982**, *55*, 1183–1187.
[c] Mustafa, A.; Hilmy, M. K. *J. Chem. Soc.* **1952**, 1339–1342.

Table 4. Reaction of *N*-sulfenyl-1,2-benzisothiazolin-3-ones **1** with thiols



Entry	**1**	R^1	R^2	Yield (%) of **7**[a]	
1	**1a**	Me	$CH_3(CH_2)_{11}$	**7a**	92
2	**1b**	Et	$CH_3(CH_2)_{11}$	**7b**	97
3	**1b**	Et	$CH_3(CH_2)_7$	**7c**	99

[a] Isolated product.

indicated that the reaction pathway of **1** can be controlled by using different nucleophiles for different purposes: hard nucleophiles such as amines and sodium salts of active methylene compounds can be used to synthesize sulfenylated compounds; soft nucleophiles such as thiols can be employed to obtain ring-opened products.

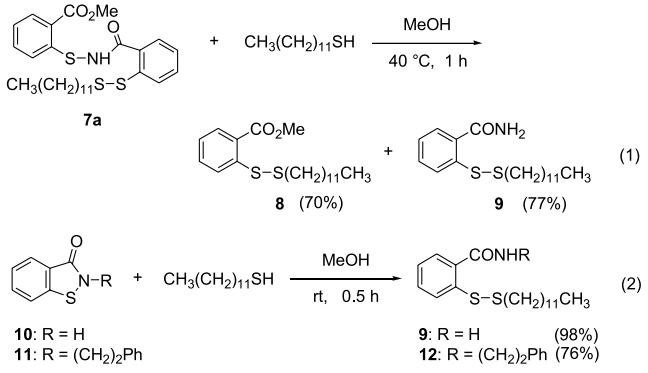
4. Experimental

4.1. General

Melting points were determined on a Mettler FP90 microscopic plate and are uncorrected. ^{1}H 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. Analytical TLC was performed on a Merck precoated TLC plate (silica gel 60 F254, 0.25 mm). Silica gel column chromatography was carried out on Merck silica gel 60 (0.063–0.200 mm). Elemental analysis and HRMS analysis were performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology. *N*-[2-(Alkoxycarbonyl)benzenesulfenyl]-1,2-benzisothiazolin-3-ones (**1**) were prepared by the method described in our previous paper.[15]

4.2. General procedure for the substitution reaction of 1a with active methylene compounds

To a suspension of NaH (0.75 mmol, 18.0 mg) in THF (5 mL) at room temperature under a nitrogen atmosphere was added a solution of active methylene compound (0.75 mmol) in 5 mL of THF. The mixture was stirred for 0.5 h. A solution of **1a** (0.50 mmol, 158.5 mg) in 5 mL of THF was then added, and after the reaction mixture was stirred for 0.5 h, water was added. Product was extracted with dichloromethane, and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: dichloromethane).



Scheme 2.

4.2.1. Diethyl 2-[2-(methoxycarbonyl)benzenesulfenyl]-malonate (2a). Colorless oil; R_f=0.23 (hexane/ethyl acetate=4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (6H, t, J=7.0 Hz), 3.93 (3H, s), 4.24 (4H, q, J=7.0 Hz), 4.82 (1H, s), 7.29 (1H, ddd, J=7.9, 7.0, 1.2 Hz), 7.45 (1H, ddd, J=8.2, 7.0, 1.5 Hz), 7.50 (1H, dd, J=8.2, 1.2 Hz), 7.92 (1H, dd, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 52.4, 54.1, 62.5, 126.4, 129.8, 130.6, 131.1, 132.4, 136.7, 166.4, 166.9; IR (neat): 2984, 1730, 1466, 1437, 1368, 1256, 1146, 1061, 1028, 747 cm^{-1}; HRMS: calcd for $C_{15}H_{18}O_6S$ 326.0824, found 326.0827.

4.2.2. Ethyl 3-hydroxy-2-[2-(methoxycarbonyl)benzenesulfenyl]-2-butenecarboxylate (2′b). Colorless crystal with mp 77.6–79.0 °C (from CH_2Cl_2–hexane); R_f=0.50 (dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (3H, t, J=7.0 Hz), 2.29 (3H, s), 3.95 (3H, s), 4.19 (2H, q, J=7.0 Hz), 7.06 (1H, dd, J=8.2, 1.2 Hz), 7.14 (1H, ddd, J=7.6, 7.3, 1.2 Hz), 7.38 (1H, ddd, J=8.2, 7.3, 1.5 Hz), 8.02 (1H, dd, J=7.6, 1.5 Hz), 13.96 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 20.8, 52.1, 61.6, 91.8, 123.9, 124.7, 126.1, 131.5, 132.4, 143.0, 166.8, 173.0, 185.0; IR (KBr): 2984, 2957, 1717, 1628, 1589, 1333, 1250, 745 cm^{-1}; Anal. calcd for $C_{14}H_{16}O_5S$: C, 56.74; H, 5.44. Found: C, 57.04; H, 5.32.

4.2.3. 3-Hydroxy-2-[2-(methoxycarbonyl)benzenesulfenyl]-1-phenyl-2-buten-1-one (2′c). Yellow crystal with mp 141.2–142.5 °C (from CH_2Cl_2–hexane); R_f=0.38 (hexane/ethyl acetate=4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (3H, s), 3.90 (3H, s), 7.19 (1H, t, J=8.2 Hz), 7.26–7.30 (3H, m), 7.39 (1H, t, J=7.7 Hz), 7.48 (1H, td, J=7.7, 1.8 Hz), 7.61 (2H, dd, J=8.2, 1.8 Hz), 8.02 (1H, dd, J=7.3, 1.8 Hz), 17.84 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 52.1, 100.9, 124.3, 124.6, 126.2, 127.8, 128.4, 131.2,

131.9, 133.0, 135.4, 143.4, 166.5, 190.6, 203.6; IR (KBr): 3063, 3003, 2951, 1715, 1588, 1535, 1460, 1435, 1269, 1252, 745, 694 cm^{-1}; Anal. calcd for $C_{18}H_{16}O_4S$: C, 65.84; H, 4.91. Found: C, 65.85; H, 4.71.

4.2.4. 4-Hydroxy-3-[2-(methoxycarbonyl)benzenesulfenyl]-3-penten-2-one (2′d). Colorless crystal with mp 116.0–117.0 °C (from CH_2Cl_2–hexane); R_f=0.50 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 2.29 (6H, s), 3.96 (3H, s), 7.06 (1H, dd, J=8.2, 1.2 Hz), 7.19 (1H, ddd, J=7.9, 7.3, 1.2 Hz), 7.42 (1H, ddd, J=8.2, 7.3, 1.5 Hz), 8.07 (1H, dd, J=7.9, 1.5 Hz), 17.38 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.3, 52.2, 101.5, 124.0, 124.3, 126.2, 132.0, 133.0, 142.5, 166.7, 198.6; IR (KBr): 2957, 1713, 1593, 1562, 1462, 1437, 1275, 1256 cm^{-1}; Anal. calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30. Found: C, 58.63; H, 5.15.

4.2.5. Ethyl 2-cyano-2-[2-(methoxycarbonyl)benzenesulfenyl]acetate (2e). Colorless crystal with mp 67.3–68.3 °C (from CH_2Cl_2–hexane); R_f=0.37 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (3H, t, J=7.0 Hz), 3.95 (3H, s), 4.30 (2H, qd, J=7.0, 0.9 Hz), 4.86 (1H, s), 7.42 (1H, ddd, J=7.6, 7.3, 1.2 Hz), 7.56 (1H, ddd, J=8.2, 7.3, 1.5 Hz), 7.63 (1H, dd, J=8.2, 1.2 Hz), 7.98 (1H, dd, J=7.6, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 39.0, 52.7, 63.9, 114.1, 128.1, 131.4, 131.5, 131.6, 132.9, 133.5, 163.2, 166.8; IR (KBr): 2988, 2955, 2907, 1746, 1709, 1289, 1260, 745 cm^{-1}; Anal. calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69; N, 5.01. Found: C, 55.98; H, 4.51; N, 4.91.

4.2.6. 2-(Benzenesulfonyl)-2-[2-(methoxycarbonyl)benzenesulfenyl]acetonitrile (2f). Yellow oil; R_f=0.36 (dichloromethane/ethyl acetate=4:1); ^1H NMR (500 MHz, $CDCl_3$): δ 5.34 (1H, s), 7.49 (1H, td, J=7.6, 1.2 Hz), 7.55 (1H, td, J=7.6, 1.8 Hz), 7.66 (2H, td, J=7.6, 1.2 Hz), 7.76 (1H, dd, J=7.6, 1.2 Hz), 7.79 (1H, td, J=7.6, 1.2 Hz), 7.92 (1H, dd, J=7.6, 1.8 Hz), 8.09 (2H, dd, J=7.6, 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.9, 60.5, 112.2, 129.5, 129.8, 130.4, 131.0, 131.3, 132.8, 133.8, 134.8, 135.0, 135.6, 166.8; IR (neat): 3067, 2957, 2924, 1711, 1586, 1449, 1337, 1290, 1262, 1159, 748, 685, 588 cm^{-1}; HRMS: calcd for $C_{16}H_{13}NO_4S_2$ 347.0286, found 347.0250.

4.3. General procedure for reaction of 1 with Grignard reagents

To a solution of **1** (0.5 mmol) in THF (10 mL) at room temperature was added a Grignard reagent (1.0 M in THF, 0.7 mL) under a nitrogen atmosphere. The mixture was stirred for 2 h, and then water was added to the reaction mixture. Product was extracted with dichloromethane, and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: 1:1 dichloromethane/hexane, dichloromethane, 100:5:1 dichloromethane/acetone/methanol).

4.3.1. Ethyl 2-(methylthio)benzoate (3a). Colorless oil;[15] R_f=0.67 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.40 (3H, t, J=7.3 Hz), 2.45 (3H, s), 4.39 (2H, q, J=7.3 Hz), 7.15 (1H, ddd, J=8.5, 7.6, 0.9 Hz), 7.27 (1H, d, J=7.9 Hz), 7.47 (1H, ddd, J=8.5, 7.9, 1.5 Hz), 8.01 (1H, dd, J=7.6, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 15.3, 60.7, 123.1, 124.0, 126.8, 130.9, 132.1, 142.8, 166.1; IR (KBr): 1709, 1246, 1062, 742 cm^{-1}.

4.3.2. *N*,*N*-Bis[2-(ethoxycarbonyl)benzenesulfenyl]-2-(methylthio)benzamide (4a). Colorless crystal with mp 165.4–166.9 °C (from dichloromethane–hexane); R_f=0.50 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (6H, t, J=7.0 Hz), 2.55 (3H, s), 4.35 (4H, q, J=7.0 Hz), 6.99 (1H, td, J=7.6, 1.2 Hz), 7.17(1H, dd, J=7.6, 1.2 Hz), 7.26 (4H, t, J=6.1 Hz), 7.40 (1H, d, J=7.3 Hz), 7.66 (2H, t, J=7.3 Hz), 7.80 (1H, brs), 8.01 (2H, d, J=7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 18.5, 61.6, 123.4, 124.0, 124.9, 125.0, 125.9, 129.9, 130.4, 131.0, 133.4, 134.9, 137.5, 166.6, 175.8; IR (KBr): 1688, 1310, 1176, 1275, 1101, 749 cm^{-1}; Anal. calcd for $C_{26}H_{25}NO_5S_3$: C, 59.18; H, 4.78; N, 2.65. Found: C, 59.40; H, 4.60; N, 2.59.

4.3.3. Ethyl 2-(benzylthio)benzoate (3b). Colorless crystal with mp 69.6–70.2 °C (from hexane) (lit.[16] 68.5–69 °C); R_f=0.67 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.38 (3H, t, J=7.2 Hz), 4.16 (2H, s), 4.37 (2H, q, J=7.2 Hz), 7.16 (1H, ddd, J=7.8, 7.0, 1.2 Hz), 7.25 (1H, ddd, J=7.6, 7.0, 1.5 Hz), 7.29–7.34 (3H, m), 7.39 (1H, dd, J=7.6, 1.5 Hz), 7.40–7.44 (2H, m), 7.97 (1H, dd, J=7.8, 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 37.5, 61.3, 124.2, 126.1, 127.5, 128.1, 128.7, 129.2, 131.3, 132.4, 136.3, 141.9, 166.6; IR (neat): 2978, 1705, 1277, 1250, 1148, 1063, 734, 712 cm^{-1}.

4.3.4. *N*,*N*-Bis[2-(ethoxycarbonyl)benzenesulfenyl]-2-(benzylthio)benzamide (4b). Colorless crystal with mp 150.2–151.6 °C (from ethyl acetate–hexane); R_f=0.50 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (6H, t, J=7.0 Hz), 4.21 (2H, s), 4.26–4.33 (4H, m), 7.02 (1H, td, J=7.6, 0.9 Hz), 7.13–7.34 (13H, m), 7.63 (1H, brs), 8.00 (2H, d, J=5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 41.2, 61.6, 123.5, 124.0, 124.8, 124.9, 127.2, 127.3, 128.5, 129.4, 129.6, 131.0, 132.1, 133.4, 134.1, 137.1, 140.0, 143.6, 166.6, 176.0; IR (KBr) 1687, 1312, 1277, 1104, 747 cm^{-1}; Anal. calcd for $C_{32}H_{29}NO_5S_3$: C, 63.66; H, 4.84; N, 2.32. Found: C, 63.82; H, 4.71; N, 2.34.

4.3.5. Ethyl 2-(phenylthio)benzoate (3c). Colorless oil;[17] R_f=0.67 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.42 (3H, t, J=7.2 Hz), 4.42 (2H, q, J=7.2 Hz), 6.82 (1H, dd, J=8.1, 1.1 Hz), 7.13 (1H, td, J=7.6, 1.1 Hz), 7.24 (2H, ddd, J=8.5, 7.3, 1.5 Hz), 7.41–7.44 (3H, m), 7.56 (2H, dt, J=7.9, 2.4 Hz), 7.99 (1H, dd, J=7.9, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 61.3, 124.3, 127.2, 127.5, 129.0, 129.7, 131.0, 132.2, 132.7, 135.5, 143.0, 166.5; IR (KBr): 1711, 1250, 742 cm^{-1}.

4.3.6. *N*,*N*-Bis[2-(ethoxycarbonyl)benzenesulfenyl]-2-(phenylthio)benzamide (4c). Colorless crystal with mp 197.0–200.0 °C (from dichloromethane–hexane); R_f=0.50 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (6H, t, J=7.2 Hz), 4.32 (4H, q, J=7.0 Hz), 7.07 (1H, td, J=7.5, 1.2 Hz), 7.02–7.34 (11H, m), 7.41 (2H, dd, J=7.0, 1.5 Hz), 7.58 (1H, brs), 8.00 (2H, d, J=7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 61.5, 123.3, 124.0, 124.9, 125.5, 127.1, 129.2, 130.1, 130.7, 131.0, 132.6, 133.4, 133.5,

135.7, 138.6, 166.6, 175.5; IR (KBr): 2980, 1687, 1462, 1278, 1059, 744 cm^{-1}; Anal. calcd for $C_{31}H_{27}NO_5S_3$: C, 63.13; H, 4.61; N, 2.38. Found: C, 62.81; H, 4.50; N, 2.23.

4.3.7. Methyl 2-(phenylthio)benzoate (3d). Colorless oil; (lit.[18] bp 140 °C/120 Pa); R_f=0.67 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 3.95 (3H, s), 6.82 (1H, d, J=8.2 Hz), 7.12 (1H, ddd, J=7.9, 7.3, 1.2 Hz), 7.23 (1H, ddd, J=8.2, 7.3, 1.5 Hz), 7.41–7.43 (3H, m), 7.55–7.57 (2H, m), 7.97 (1H, dd, J=8.2, 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.1, 124.3, 126.7, 127.4, 129.0, 129.7, 131.0, 132.2, 132.5, 135.5, 143.1, 166.8; IR (neat): 1717, 1435, 1250, 1059, 743 cm^{-1}.

4.3.8. *N*,*N*-Bis[2-(methoxycarbonyl)benzenesulfenyl]-2-(phenylthio)benzamide (4d). Colorless crystal with mp 197.7–199.3 °C (from ethyl acetate–hexane); R_f=0.50 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 3.86 (6H, s), 7.07 (1H, td, J=7.5, 1.2 Hz), 7.20–7.32 (11H, m), 7.41 (2H, d, J=7.3 Hz), 7.58 (1H, brs), 7.98 (2H, d, J=7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.5, 123.4, 123.7, 125.0, 125.5, 127.1, 129.2, 130.2, 130.7, 131.1, 132.7, 133.6, 133.6, 135.8, 138.6, 175.5, 178.2, 190.5, 196.9; IR (KBr): 1680, 1314, 1281, 1424, 747 cm^{-1}; Anal. calcd for $C_{29}H_{23}NO_5S_3$: C, 62.01; H, 4.13; N, 2.49. Found: C, 62.21; H, 3.92; N, 2.51.

4.4. X-ray crystallographic analysis of 4b

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 **4b**: $C_{32}H_{29}NO_5S_3$, M=603.76, monoclinic, space group $P2_1/n$, a=11.138(2), b=16.692(2), c=16.453(3) Å, β=98.99(2)°, V=3021.3(9) $Å^3$, T=173.2 K, Z=4, D_{calc}=1.327 g cm^{-3}, μ=0.286 mm^{-1}; goodness of fit=1.005; $R1$ [$I>2\sigma(I)$]=0.038, $wR2$=0.145 (all data).

Selected bond distances (Å) and angles (°) are shown as follows: S(1)–N(1) 1.722(1), S(1)–C(8) 1.777(2), S(2)–N(1) 1.714(1), S(2)–C(17) 1.774(2), O(1)–C(7) 1.203(2), N(1)–C(7) 1.404(2), C(1)–C(7) 1.512(2); S(1)–N(1)–S(2) 117.76(7), S(1)–N(1)–C(7) 120.9(1), C(8)–S(1)–N(1) 101.50(6), S(2)–N(1)–C(7) 120.3(1), C(17)–S(2)–N(1) 101.02(7), O(1)–C(7)–N(1) 121.9(1), O(1)–C(7)–C(1) 123.3(1). Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 243897. 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].

4.5. General procedure for the reaction of 5 with Grignard reagents

To a solution of **5** (0.5 mmol) in THF (10 mL) at room temperature was added a Grignard reagent (1 M in THF, 0.7 mL) under nitrogen atmosphere. The mixture was stirred for 2 h, and then water was added to the reaction mixture. Product was extracted with dichloromethane, and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: dichloromethane, 10:1 dichloromethane/ethyl acetate).

4.5.1. *N*-Phenyl-2-(methylthio)benzamide (6a). Colorless crystal with mp 146.7–147.5 °C (from ethyl acetate–hexane) (lit.[13] 148–149 °C); R_f=0.70 (dichloromethane/ethyl acetate=10:1); ^1H NMR (500 MHz, $CDCl_3$): δ 2.50 (3H, s), 7.16 (1H, t, J=7.3 Hz), 7.28 (2H, t, J=7.6 Hz), 7.36–7.45 (4H, m), 7.66 (2H, d, J=7.3 Hz), 7.74 (1H, d, J=7.6 Hz), 8.31 (1H, brs); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 120.0, 124.5, 125.6, 127.9, 129.0, 129.3, 131.0, 132.3, 136.6, 137.9, 166.0; IR (KBr): 3300, 1649, 1601 cm^{-1}.

4.5.2. *N*-Phenyl-2-(phenylthio)benzamide (6b). Colorless crystal with mp 118.7–119.0 °C (from ethyl acetate–hexane); R_f=0.45 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 7.13 (1H, tt, J=7.3, 1.2 Hz), 7.26–7.37 (10H, m), 7.52 (2H, d, J=7.9 Hz), 7.78 (1H, d, J=8.5 Hz), 8.20 (1H, brs); ^{13}C NMR (125 MHz, $CDCl_3$): δ 120.0, 124.6, 127.5, 127.8, 129.0, 129.6, 131.2, 131.6, 132.7, 134.1, 134.4, 136.9, 137.7, 165.6; IR (KBr): 3354, 1664, 1597 cm^{-1}; Anal. calcd for $C_{19}H_{15}NOS$: C, 74.72; H, 4.95; N, 4.59. Found: C, 74.70; H, 4.82; N, 4.69.

4.5.3. *N*-(*p*-Methylphenyl)-2-(methylthio)benzamide (6c). Colorless crystal with mp 144.1–145.5 °C (from ethyl acetate–hexane) (lit.[13] 145–146 °C); R_f=0.60 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 2.33 (3H, s), 2.47 (3H,s), 7.16 (2H, d, J=8.1 Hz), 7.25 (1H, td, J=7.3, 1.2 Hz), 7.36 (1H, dd, J=7.9, 1.2 Hz), 7.41 (1H, ddd, J=7.9, 7.3, 1.5 Hz), 7.53 (2H, d, J=8.1 Hz), 7.69 (1H, d, J=7.3 Hz), 8.29 (1H, brs); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.0, 20.9, 120.0, 125.7, 128.0, 129.1, 129.5, 130.9, 134.2, 135.3, 135.3, 136.5, 165.8; IR (KBr): 3281, 1649, 1602 cm^{-1}.

4.5.4. *N*-(2-Phenylethyl)-2-(methylthio)benzamide (6d). Colorless crystal with mp 118.1–118.6 °C (from ethyl acetate–hexane); R_f=0.33 (dichloromethane/ethyl acetate=20:1); ^1H NMR (500 MHz, $CDCl_3$): δ 2.39 (3H, s), 2.94 (2H, t, J=7.2 Hz), 3.70 (2H, td, J=7.2, 5.8 Hz), 6.49 (1H, brs), 7.13 (1H, ddd, J=8.2, 7.3, 1.2 Hz), 7.21–7.36 (8H, m), 7.44 (1H, dd, J=7.8, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.6, 35.5, 41.1, 125.1, 126.5, 127.0, 128.3, 128.6, 128.8, 130.6, 135.0, 137.0, 138.9, 168.1; IR (KBr): 3308, 1632, 1541 cm^{-1}; Anal. calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.90; H, 6.24; N, 5.30.

4.6. General procedure for reaction of 1 with thiols

To a solution of **1** (0.5 mmol) in methanol (10 mL) at room temperature was added thiol (0.5 mmol). The mixture was stirred for 0.5 h, and then the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: dichloromethane).

4.6.1. *N*-[2-(Methoxycarbonyl)benzenesulfenyl]-2-(dodecyldithio)benzamide (7a). Colorless crystal with mp 79.5–80.3 °C (from ethyl acetate–hexane); R_f=0.38 (dichloromethane); ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, J=6.7 Hz), 1.24–1.36 (18H, m), 1.64–1.70 (2H, m), 2.75 (2H, t, J=7.4 Hz), 3.95 (3H, s), 7.20–7.32 (3H, m),

7.47–7.53 (3H, m), 7.69 (1H, s), 8.00–8.04 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 28.5, 28.9, 29.2, 29.3, 29.5, 29.58, 29.63, 31.9, 38.8, 52.5, 122.5, 124.3, 124.7, 126.6, 128.0, 128.7, 131.1, 131.6, 133.1, 133.5, 138.2, 144.5, 167.1, 169.3; IR (KBr): 3268, 2955, 2922, 2851, 1701, 1632, 1470, 1422, 1318, 1292, 1246, 739 cm^{-1}; Anal. calcd for $C_{27}H_{37}NO_3S_3$: C, 62.39; H, 7.17; N, 2.69. Found: C, 62.56; H, 7.19; N, 2.61.

4.6.2. *N*-[2-(Ethoxycarbonyl)benzenesulfenyl]-2-(dodecyldithio)benzamide (7b). Colorless crystal with mp 47.2–48.5 °C (from hexane); R_f=0.38 (dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (3H, t, J=7.0 Hz), 1.23–1.35 (18H, m), 1.41 (3H, t, J=7.3 Hz), 1.66 (2H, quint, J=7.3 Hz), 2.74 (2H, t, J=7.3 Hz), 4.40 (2H, q, J=7.0 Hz), 7.20 (1H, ddd, J=8.2, 6.7, 1.5 Hz), 7.29–7.34 (2H, m), 7.47–7.50 (3H, m), 7.69 (1H, brs), 8.00–8.01 (1H, m), 8.03 (1H, d, J=7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 14.3, 22.7, 28.5, 28.9, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 38.8, 61.6, 122.4, 124.6, 124.7, 126.5, 128.6, 131.1, 131.6, 133.0, 133.5, 138.3, 144.4, 166.7, 169.4; IR (KBr): 3235, 1696, 1661, 1420, 1275, 1150, 1103, 1057, 749 cm^{-1}; Anal. calcd for $C_{28}H_{39}NO_3S_3$: C, 63.00; H, 7.36; N, 2.62. Found: C, 63.39; H, 7.43; N, 2.57.

4.6.3. *N*-[2-(Ethoxycarbonyl)benzenesulfenyl]-2-(octyldithio)benzamide (7c). Colorless oil; R_f=0.38 (dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (3H, t, J=7.3 Hz), 1.24–1.31 (8H, m), 1.35–1.37 (2H, m), 1.40 (3H, t, J=7.0 Hz), 1.63–1.69 (2H, m), 2.73 (2H, t, J=7.3 Hz), 4.39 (2H, q, J=7.0 Hz), 7.19 (1H, td, J=7.9, 1.5 Hz), 7.27 (1H, m), 7.40–7.49 (4H, m), 7.68 (1H, brs), 7.99–8.01 (1H, m), 8.02 (1H, d, J=7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 14.3, 22.6, 28.4, 28.8, 29.1, 31.7, 38.7, 61.5, 122.4, 124.5, 124.6, 126.4, 128.4, 131.0, 131.5, 133.0, 133.3, 133.3, 144.5, 166.6, 169.3; IR (neat): 3266, 1696, 1466, 1433, 1273, 1103, 741 cm^{-1}; HRMS: calcd for $C_{24}H_{31}NO_3S_3$ 477.1466. Found 477.1422.

4.7. Procedure for the reaction of 7a with 1-dodecanethiol

To a solution of **7a** (0.5 mmol, 259.9 mg) in methanol (10 mL) was added 1-dodecanethiol (0.5 mmol, 101.2 mg). The mixture was stirred at 40 °C for 0.5 h, and then the solvent was removed under reduced pressure. The crude products were purified by silica gel column chromatography (eluent: 1:1 dichloromethane/hexane).

4.7.1. Methyl 2-(dodecyldithio)benzoate (8). Colorless oil;[19] R_f=0.70 (dichloromethane/hexane=1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, J=6.8 Hz), 1.24–1.36 (18H, m), 1.63–1.69 (2H, m), 2.71 (2H, t, J=7.6 Hz), 3.94 (3H, s), 7.21–7.26 (1H, m), 7.55 (1H, ddd, J=8.9, 7.3, 1.5 Hz), 8.01 (1H, dd, J=7.8, 1.5 Hz), 8.18 (1H, d, J=8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 28.6, 29.0, 29.2, 29.3, 29.5, 29.57, 29.63, 31.9, 38.5, 52.2, 125.0, 125.7, 127.0, 131.4, 132.7, 142.2, 166.8; IR (KBr): 2926, 2853, 1715, 1460, 1435, 1269, 1252, 1144, 1101, 1053, 745 cm^{-1};

4.7.2. 2-(Dodecyldithio)benzamide (9). Colorless crystal with mp 120.0–121.4 °C (from ethyl acetate–hexane); R_f=0.45 (dichloromethane/acetone/methanol=100:10:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, J=7.0 Hz), 1.28–1.37 (18H, m), 1.66 (2H, quint, J=7.3 Hz), 2.73 (2H, t, J=7.3 Hz), 7.49 (1H, ddd, J=8.2, 7.3, 1.2 Hz), 7.58 (1H, dd, J=7.6, 1.2 Hz), 8.04 (1H, dd, J=8.2, 0.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 28.6, 29.0, 29.2, 29.4, 29.5, 29.59, 29.64, 31.9, 38.8, 126.0, 127.9, 128.3, 131.4, 132.9, 138.5, 169.5; IR (KBr): 3372, 3185, 2953, 2920, 2851, 1649, 1616, 1464, 1406, 1103 cm^{-1}; Anal. calcd for $C_{19}H_{31}NOS_2$: C, 64.54; H, 8.84; N, 3.96. Found: C, 64.74; H, 8.91; N, 3.86.

4.8. Procedure for the reactions of 10 or 11 with 1-dodecanethiol

To a solution of **10** or **11** (0.5 mmol) in methanol (10 mL) at room temperature was added 1-dodecanethiol (0.5 mmol, 101.2 mg). The mixture was stirred for 0.5 h, and then the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: dichloromethane).

4.8.1. *N*-(2-Phenylethyl)-2-(dodecyldithio)benzamide (12). Colorless crystal with mp 71.4–72.3 °C (from dichloromethane–hexane); R_f=0.50 (dichloromethane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, J=6.7 Hz), 1.24–1.35 (18H, m), 1.61–1.67 (2H, m), 2.70 (2H, t, J=7.4 Hz), 2.96 (2H, t, J=6.7 Hz), 3.71–3.75 (2H, m), 6.08 (1H, brs), 7.18–7.44 (8H, m), 7.96 (1H, d, J=8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 28.5, 28.9, 29.2, 29.3, 29.5, 29.59, 29.63, 31.9, 35.6, 38.8, 41.2, 126.1, 126.6, 127.7, 128.7, 128.9, 130.8, 134.5, 137.6, 138.8, 167.7; IR (KBr): 3318, 3065, 3032, 2920, 2851, 1630, 1537, 1456, 1313, 1194, 745, 696 cm^{-1}; Anal. calcd for $C_{27}H_{39}NOS_2$: C, 70.85; H, 8.59; N, 3.06. Found: C, 71.02; H, 8.48; N, 2.85.

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