SYNTHESIS OF 1,2-BENZOTHIAZOLE-3(2H)-THIONE 1,1-DIOXIDES
BY DBU-PROMOTED CYCLIZATION OF 2-(AMINOSULFONYL)-N-
METHYLBENZOTHIOAMIDE DERIVATIVES

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Abstract – An efficient method for the preparation of 2-alkyl-1,2-benzothiazole-3(2H)-thione 1,1-dioxides has been developed. Thus, the reaction of 2,N-dilithio derivatives of N-alkylbenzenesulfonamides with methyl isothiocyanate affords 2-[(alkylamino)sulfonyl]-N-methylbenzothioamides, which are treated with a catalytic amount of DBU in refluxing toluene to provide the desired products in moderate to good yields.

Some compounds having the 1,2-benzothiazole-3(2H)-thione 1,1-dioxide structure (thiosaccharin) have been reported to be versatile as agricultural or horticultural plant disease control agents or pesticides. Thiocarbonylation of the carbonyl function of 1,2-benzothiazol-3(2H)-one 1,1-dioxides (saccharins) with awkward sulfurization agents, such as P2S5 and Lawesson’s reagent, has traditionally been used for the synthesis of this type of heterocycles. Accordingly, development of a facile route for the synthesis of these heterocycles using inexpensive and easily handling reagents is of considerable merit. In connection of our ongoing investigations on the synthesis of heterocycles utilizing the reactions of o-functionalized phenyllithiums with isothiocyanates, we have recently reported that 1,2-benzothiazol-3(2H)-imine 1,1-dioxide and 4H-1,3,2-benzodithiazin-4-imine 1,1-dioxide derivatives can be obtained on exposure of 2-(aminosulfonyl)benzothioamides, derived from the reaction of 2,N-dilithiobenzenesulfonamides with isothiocyanates, to thionyl chloride and iodine, respectively. In this manuscript, we wish to report an efficient method for the preparation of 2-alkyl-1,2-benzothiazole-3(2H)-thione 1,1-dioxides (3). The synthesis involves the formation of 2-[(alkylamino)sulfonyl]-N-methylbenzothioamides (2) utilizing the
reaction of \(N\)-alkyl-2,\(N\)-dilithiobenzenesulfonamides, generated from \(N\)-alkylbenzenesulfonamides (1) and two equivalents of butyllithium, with methyl isothiocyanate followed by ring closure with a help of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

![Scheme 1](image)

### Table 1. Preparation of \(2H\)-1,2-benzothiazole-3(2\(H\))-thione 1,1-dioxides (3)

<table>
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<tr>
<th>Entry</th>
<th>1</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>2</th>
<th>Yield/%(^a)</th>
<th>3</th>
<th>Yield/%(^a)</th>
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<td>H</td>
<td>Me</td>
<td>2a</td>
<td>58(^b)</td>
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<tr>
<td>2</td>
<td>1b</td>
<td>Me</td>
<td>Me</td>
<td>2b</td>
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<td>85</td>
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<tr>
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<td>(n)-Bu</td>
<td>2c</td>
<td>60(^b)</td>
<td>3c</td>
<td>73</td>
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<td>(i)-Bu</td>
<td>2d</td>
<td>66</td>
<td>3d</td>
<td>63</td>
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<td>Me</td>
<td>CH(_2)=CHCH(_2)</td>
<td>2e</td>
<td>61</td>
<td>3e</td>
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<td>36</td>
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<td>Et</td>
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<td>51(30(^b))</td>
<td>3j</td>
<td>87</td>
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<tr>
<td>11</td>
<td>1k</td>
<td>OMe</td>
<td>Me</td>
<td>2k</td>
<td>83</td>
<td>3k</td>
<td>53(^d)</td>
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</table>

\(^a\) Yields of isolate products. \(^b\) See ref. 5. \(^c\) Compound 3i\(^c\) was obtained in 32% yield. \(^d\) Compound 3k\(^c\) was obtained in 10% yield.

The preparation of benzothiazolethione 1,1-dioxides (3) was carried out as illustrated in Scheme 1. As the first step of the present sequence, \(N\)-substituted benzenesulfonamides (1) were treated with two equivalents of butyllithium in THF at 0 °C and the resulting 2,\(N\)-dilithio products were allowed to react with methyl isothiocyanate at the same temperature. The corresponding 2-(aminosulfonyl)benzothioamides (2) were obtained in moderate to good yields, as summarized in Table 1. Treatment of 2 with 0.1 equivalent of DBU in toluene at reflux temperature afforded the desired products (3). The results obtained are summarized in Table 1 as well. As can be seen from it, transformation of 2 into 3 can be accomplished in generally fair to good yields. Under these reaction conditions, \(N\)-methyl-2-[(phenylamino)sulfonyl]benzothioamide (2i) did not afford the corresponding desired product.
(3i) at all and 5,5(E)-N-dimethyl-2-phenyl-1,2-benzothiazol-3(2H)-imine 1,1-dioxide (3i') was alternatively obtained in 32% yield (Entry 9), though the reason for this result is not clear yet. The reaction using 2j afforded the desired products in 53% yield along with 10% yield of the corresponding 1,2-benzothiazol-3(2H)-imine 1,1-dioxide (3k') (Entry 11). These products were easily separated from each other by column chromatography on silica gel. The use of 1,4-diazabicyclo[2.2.2]octane (DABCO) in place of DBU gave comparable results. The progress of the reactions using triethylamine was sluggish and considerable amounts of 2 were recovered after extended reaction times.

\[
\begin{align*}
\text{Scheme 2} & \\
4 & \text{SO} \quad \text{NHR} & \begin{array}{c}
\text{1. } n\text{-BuLi (2 eq.), THF, } 0 \degree \text{C} \\
\text{2. } \text{MeNCS, } 0 \degree \text{C} \\
\text{3. } \text{H}_3\text{O}^+ \\
\end{array} & \text{SO} \quad \text{O} & \text{N-R} \\
5a & \text{R} = \text{Me} & 63\% \\
5b & \text{R} = \text{Et} & 62\% \\
5c & \text{R} = \text{Ph} & 56\%
\end{align*}
\]

Subsequently, the preparation of 2-substituted naphtho[2,1-d][1,2]thiazole-3(2H)-thione 1,1-dioxides (5) utilizing a similar sequence as mentioned above starting with N-substituted naphthalene-1-sulfonamides (4) was attempted. As shown in Scheme 2, these sulfonamides (4) were di-lithiated and allowed to react with methyl isothiocyanate as described above to give, after aqueous workup, the corresponding desired products (5) directly in moderate-to-fair yields. It is notable that the cyclization reaction of the initially formed 2-(aminosulfonyl)naphthalene-1-carbothioamides took place during workup and/or purification by column chromatography on silica gel.

\[
\begin{align*}
\text{Scheme 3} & \\
6 & \text{SO} \quad \text{NHMe} & \begin{array}{c}
\text{1. } n\text{-BuLi (2 eq.), THF, } 0 \degree \text{C} \\
\text{2. } \text{MeNCS, } 0 \degree \text{C} \\
\end{array} & \begin{array}{c}
\text{SO} \quad \text{NHMe} \\
\text{NHMe} \\
\text{SO} \quad \text{NHMe} \\
\text{SO} \quad \text{NHMe} \\
\end{array} & \begin{array}{c}
7a \\
7b \\
\end{array} & \text{DBU (0.1 eq.), toluene, reflux} \\
\text{8a} & \text{32\% (80:20)} \\
\text{8b}
\end{align*}
\]
When N-methylnaphthalene-2-sulfonamide (6) was exposed to the same reaction conditions, the direct production of the corresponding naphthothiazolethiones (8) was not achieved. The crude products including 1- and 3-(methylsulfonyl)naphthalene-2-carbothioamides (7a) and (7b) underwent cyclization with DBU as described above to afford an inseparable mixture of 2-methylnaphtho[1,2-d][1,2]thiazol-3(2H)-one 1,1-dioxide (8a) and 2-methylnaphtho[2,3-d][1,2]thiazol-3(2H)-one 1,1-dioxide (8b) in 32% overall yield from 6, as depicted in Scheme 3.

In conclusion, an efficient method has been developed for the preparation of 1,2-benzothiazole-3(2H)-thione 1,1-dioxide (thiosaccharin) derivatives by the reaction of 2,N-dilithio compounds of secondary benzenesulfonamides with methyl isothiocyanate followed by cyclization of the resulting 2-(aminosulfonyl)-N-methylbenzothioamides with elimination of methylamine. The present method has advantages in the ready availability of the starting materials and the simplicity of the operations and its additional feature is the use of safe and inexpensive ordinary reagents.

**EXPERIMENTAL**

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a PerkinElmer Spectrum 65 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 and 125 MHz, respectively. High-resolution MS spectra were measured by a Thermo Scientific Exactive spectrometer (DART). Elemental analyses were performed with an Elementar Vario EL II instrument. TLC was carried out on Merck Kieselgel 60 PF₂₅₄. Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

**Starting Materials.** N-Substituted benzenesulfonamides (1d–1g), (1g), (1k), N-substituted 2-[(methylamino)sulfonyl]benzothioamides (2a), (2c), (2j), and N-substituted naphthalene-1-sulfonamides (4a), (4c) were prepared according to the reported procedures. n-BuLi was supplied by Asia Lithium Corporation. All other chemicals used in this study were commercially available.

N-Methyl-2-(aminosulfonyl)benzothioamides (2b), (2d–i), and (2k) were prepared from the respective benzenesulfonamides and MeNCS according to the procedure described for the synthesis of 2a.

**5,N-Dimethyl-2-[(methylamino)sulfonyl]benzothioamide (2b):** a pale-yellow solid; mp 161–163 °C (hexane/CH₂Cl₂); IR (KBr) 3281, 3201, 1367, 1167 cm⁻¹; ¹H NMR δ 2.42 (s, 3H), 2.52 (d, J = 5.7 Hz, 3H), 3.31 (d, J = 5.2 Hz, 3H), 5.66 (q, J = 5.7 Hz, 1H), 7.10 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 8.45 (br s, 1H); ¹³C NMR δ 21.3, 29.4, 33.2, 128.8, 129.2, 129.8, 130.3, 141.4, 144.2, 199.2. Anal. Calcd for C₁₀H₁₄N₂O₂S₂: C, 46.49; H, 5.46; N, 10.84; S, 24.82. Found: C, 46.17; H, 5.45; N, 10.79; S, 24.50.
5. N-Dimethyl-2-[(2-methylpropyl)amino[sulfonyle]benzothioamide (2d): a pale-yellow solid; mp 95–97 °C (hexane/CH₂Cl₂); IR (KBr) 3273, 3146, 1324, 1166 cm⁻¹; ¹H NMR δ 0.88 (d, J = 6.3 Hz, 6H), 1.69–1.77 (m, 1H), 2.42 (s, 3H), 2.60 (dd, J = 6.9 Hz, 2H), 3.31 (d, J = 5.2 Hz, 3H), 5.79 (t, J = 6.9 Hz, 1H), 7.07 (s, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 8.55 (br s, 1H); ¹³C NMR δ 20.0, 21.3, 28.3, 33.2, 50.7, 128.6, 129.2, 129.4, 131.5, 141.2, 144.0, 199.3. Anal. Calcd for C₁₃H₂₀N₂O₂S₂: C, 51.97; H, 6.71; N, 9.32; S, 21.34. Found: C, 51.91; H, 6.93, N, 9.28; S, 21.35.

5. N-Dimethyl-2-[(prop-2-enyl)amino[sulfonyle]benzothioamide (2e): a pale-yellow solid; mp 96–98 °C (hexane/CH₂Cl₂); IR (KBr) 3298, 3173, 1324, 1164 cm⁻¹; ¹H NMR δ 2.42 (s, 3H), 3.31 (d, J = 4.6 Hz, 3H), 3.45 (dd, J = 6.3, 5.2 Hz, 2H), 5.08 (dd, J = 10.3, 1.1 Hz, 1H), 5.19 (d, J = 17.2 Hz, 1H), 5.73 (ddd, J = 17.2, 10.3, 6.3 Hz, 1H), 5.85 (t, J = 5.2 Hz, 1H), 7.10 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 8.42 (br s, 1H); ¹³C NMR δ 21.3, 33.2, 46.0, 117.7, 128.8, 129.3, 129.5, 131.5, 132.7, 141.3, 144.4, 199.2. Anal. Calcd for C₁₂H₁₀N₂O₂S₂: C, 50.68; H, 5.67; N, 9.85; S, 22.55. Found: C, 50.65; H, 5.83; N, 9.83; S, 22.80.

5. N-Dimethyl-2-[(phenylmethyl)amino[sulfonyle]benzothioamide (2f): a yellow solid; mp 133–135 °C (hexane/CH₂Cl₂); IR (KBr) 3294, 3125, 1361, 1165 cm⁻¹; ¹H NMR δ 2.42 (s, 3H), 3.30 (d, J = 5.2 Hz, 3H), 3.99 (d, J = 6.9 Hz, 2H), 6.06 (t, J = 6.9 Hz, 1H), 7.12 (s, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.22–7.28 (m, 5H), 7.59 (d, J = 8.0 Hz, 1H), 8.37 (br s, 1H); ¹³C NMR δ 21.3, 33.2, 47.5, 127.7, 128.1, 128.5, 128.8, 129.3, 129.5, 131.5, 136.1, 141.3, 144.1, 199.3. Anal. Calcd for C₁₆H₁₈N₂O₂S₂: C, 57.46; H, 5.42; N, 8.38; S, 19.17. Found: C, 57.45; H, 5.43; N, 8.41; S, 19.19.

5. N-Dimethyl-2-[(2-phenylethyl)amino[sulfonyle]benzothioamide (2g): a pale-yellow solid; mp 130–133 °C (hexane/CH₂Cl₂); IR (KBr) 3273, 3170, 1320, 1162 cm⁻¹; ¹H NMR δ 2.40 (s, 3H), 2.78 (t, J = 7.4 Hz, 2H), 3.03–3.07 (m, 2H), 3.28 (d, J = 5.2 Hz, 3H), 5.71 (t, J = 6.3 Hz, 1H), 7.09 (s, 1H), 7.13 (d, J = 6.9 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.26 (dd, J = 7.4, 6.9 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 8.31 (br s, 1H); ¹³C NMR δ 21.3, 33.2, 35.8, 44.8, 126.6, 128.5, 128.8, 128.9, 129.3, 129.5, 131.4, 137.9, 141.3, 144.1, 199.2. Anal. Calcd for C₁₇H₂₀N₂O₂S₂: C, 58.59; H, 5.79; N, 8.04; S, 18.40. Found: C, 58.50; H, 5.84; N, 7.96; S, 18.41.

2-[(2-Methoxyethyl)amino[sulfonyle]-5,N-dimethylbenzothioamide (2h): a pale-yellow solid; mp 138–140 °C (hexane/CH₂Cl₂); IR (KBr) 3289, 3177, 1321, 1162 cm⁻¹; ¹H NMR δ 2.41 (s, 3H), 3.00 (q, J = 5.2 Hz, 2H), 3.27 (s, 3H), 3.31 (d, J = 5.2 Hz, 3H), 3.42 (t, J = 5.2 Hz, 2H), 5.93 (br s, 1H), 7.13 (s, 1H), 7.20 (d, J = 7.4 Hz, 1H), 7.59 (d, J = 7.4 Hz, 1H), 8.40 (br s, 1H); ¹³C NMR δ 21.3, 33.2, 43.0, 58.7, 70.6, 129.0, 129.2, 129.3, 131.5, 141.4, 144.0, 199.1. Anal. Calcd for C₁₂H₁₈N₂O₃S₂: C, 47.66; H, 6.00; N, 9.24; S, 21.21. Found: C, 47.56; H, 6.03; N, 9.23; S, 21.36.

5. N-Dimethyl-2-[(phenylamino)sulfonyle]benzothioamide (2i): a yellow solid; mp 163–164 °C
(hexane/CH₂Cl₂); IR (KBr) 3278, 1335, 1161 cm⁻¹; ¹H NMR δ 2.35 (s, 3H), 3.38 (d, J = 5.2 Hz, 3H), 6.96 (d, J = 8.0 Hz, 1H), 7.07 (br s, 1H), 7.10–7.13 (m, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.18–7.21 (m, 4H), 7.97 (s, 1H), 8.38 (br s, 1H); ¹³C NMR δ 21.3, 33.3, 123.6, 126.1, 128.4, 128.95, 129.04, 129.5, 130.9, 136.6, 141.1, 144.4, 199.7. Anal. Calcd for C₁₅H₁₆N₂O₂S₂: C, 56.23; H, 5.03; N, 8.74; S, 20.01. Found: C, 56.11; H, 5.04; N, 8.68; S, 20.09.

**5-Methoxy-N-methyl-2-[(methylamino)sulfonyl]benzothioamide (2k):** a yellow solid; mp 140–142 °C (hexane/CH₂Cl₂); IR (KBr) 3289, 3201, 1326, 1166 cm⁻¹; ¹H NMR δ 2.49 (d, J = 5.2 Hz, 3H), 3.28 (d, J = 4.6 Hz, 3H), 3.86 (s, 3H), 5.61 (q, J = 5.2 Hz, 1H), 6.74 (d, J = 2.3 Hz, 1H), 6.82 (dd, J = 8.6, 2.3 Hz, 1H), 7.55 (d, J = 2.3 Hz, 1H), 8.59 (br s, 1H); ¹³C NMR δ 29.4, 33.2, 55.8, 113.3, 114.0, 124.8, 131.9, 143.3, 162.8, 198.6. Anal. Calcd for C₁₀H₁₄N₂O₃S₂: C, 43.78; H, 5.14; N, 10.21; S, 23.37. Found: C, 43.51; H, 5.12; N, 10.12; S, 23.60.

**Typical Procedure for the Preparation of 1,2-Benzothiazole-3(2H)-thione 1,1-Dioxides (3).**

**2-Methyl-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3a).** A solution of 1a (0.24 g, 1.0 mmol) in toluene (10 mL) containing DBU (15 mg, 0.1 mmol) was refluxed for 2 h. The cooled mixture was diluted with AcOEt (20 mL) and washed with 1% HCl (15 mL). The organic layer was dried (Na₂SO₄) and concentrated by evaporation. The residual solid was recrystallized to afford 3a (0.15 g, 72%); a yellow solid; mp 174–176 °C (hexane/CH₂Cl₂) (lit., mp 171.5–172.5 °C); IR (KBr) 1332, 1197 cm⁻¹; ¹H NMR δ 3.54 (s, 3H), 7.79–7.87 (m, 3H), 8.28 (d, J = 7.4 Hz, 1H); ¹³C NMR δ 27.7, 120.4, 126.7, 130.6, 131.3, 133.9, 134.4, 185.6.

**2,5-Dimethyl-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3b):** a yellow solid; mp 154–156 °C (hexane/CH₂Cl₂); IR (KBr) 1332, 1189 cm⁻¹; ¹H NMR δ 3.54 (s, 3H), 7.79–7.87 (m, 3H), 8.28 (d, J = 7.4 Hz, 1H); ¹³C NMR δ 3.54 (s, 3H), 7.79–7.87 (m, 3H), 8.28 (d, J = 7.4 Hz, 1H); ¹³C NMR δ 27.7, 120.4, 126.7, 130.6, 131.3, 133.9, 134.4, 185.6. HR-MS (positive). Calcd for C₉H₁₀NO₂S₂ (M+H): 228.0153. Found: m/z 228.0148. Anal. Calcd for C₉H₉NO₂S₂: C, 47.56; H, 3.99; N, 6.16; S, 28.21. Found: C, 47.56; H, 3.87; N, 6.19; S, 28.45.

**2-Butyl-5-methyl-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3c):** a yellow oil; Rf 0.40 (AcOEt/hexane 1:15); IR (neat) 1339, 1176 cm⁻¹; ¹H NMR δ 0.98 (t, J = 7.4 Hz, 3H), 1.45 (sext, J = 7.4 Hz, 2H), 1.88–1.95 (m, 2H), 2.54 (s, 3H), 4.09 (t, J = 7.4 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H); ¹³C NMR δ 13.6, 20.2, 21.9, 29.3, 42.7, 120.1, 127.1, 128.6, 130.8, 134.5, 145.7, 185.7. HR-MS (positive). Calcd for C₁₂H₁₅NO₂S₂: C, 47.56; H, 3.99; N, 6.16; S, 28.21. Found: C, 47.56; H, 3.87; N, 6.19; S, 28.45.

**5-Methyl-2-(2-methylpropyl)-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3d):** a yellow solid; mp 74–76 °C (hexane); IR (KBr) 1337, 1182 cm⁻¹; ¹H NMR δ 1.03 (d, J = 6.9 Hz, 6H), 2.48–2.58 (m including s at 2.55, 4H), 3.93 (d, J = 7.4 Hz, 2H), 7.62 (d, J = 7.4 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 8.05
(s, 1H); $^{13}$C NMR δ 20.2, 21.9, 27.2, 50.3, 120.2, 127.3, 128.4, 130.8, 134.6, 145.8, 186.8. HR-MS (positive). Caled for C$_{12}$H$_{10}$NO$_2$S$_2$ (M+H): 270.0622. Found: m/z 270.0617. Anal. Caled for C$_{12}$H$_{15}$NO$_2$S$_2$: C, 53.51; H, 5.61; N, 5.20; S, 23.80. Found: C, 53.60; H, 5.63; N, 5.10; S, 23.88.

5-Methyl-2-(prop-2-enyl)-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3e): a yellow oil; $R_f$ 0.44 (AcOEt/hexane 1:10); IR (neat) 1339, 1176 cm$^{-1}$; $^1$H NMR δ 2.55 (s, 3H), 4.72 (ddd, $J = 6.3, 1.7, 1.1$ Hz, 2H), 5.33 (ddd, $J = 10.3, 1.7, 1.1$ Hz, 1H), 5.45 (ddd, $J = 17.2, 1.7, 1.1$ Hz, 1H), 5.94–6.02 (m, 1H), 7.63 (d, $J = 8.6$ Hz, 1H), 7.72 (d, $J = 8.6$ Hz, 1H), 8.06 (s, 1H); $^{13}$C NMR δ 21.9, 44.6, 120.19, 120.21, 127.1, 128.6, 129.4, 130.7, 134.7, 145.8, 185.4. HR-MS (positive). Caled for C$_{11}$H$_{12}$NO$_2$S$_2$ (M+H): 254.0309. Found: m/z 254.0304. Anal. Caled for C$_{11}$H$_{11}$NO$_2$S$_2$: C, 52.15; H, 4.38; N, 5.33. Found: C, 52.22; H, 4.63; N, 5.51.

5-Methyl-2-(phenylmethyl)-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3f): a yellow solid; mp 137–139 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1335, 1176 cm$^{-1}$; $^1$H NMR δ 2.53 (s, 3H), 5.26 (s, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.50 (d, $J = 7.4$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 8.04 (s, 1H); $^{13}$C NMR δ 21.9, 45.8, 120.3, 127.1, 128.0, 128.5, 128.6 (2 overlapped Cs), 130.7, 133.9, 134.7, 145.9, 185.9. HR-MS (positive). Caled for C$_{13}$H$_{14}$NO$_2$S$_2$ (M+H): 304.0466. Found: m/z 304.0459. Anal. Caled for C$_{15}$H$_{13}$NO$_2$S$_2$: C, 59.38; H, 4.32; N, 4.62; S, 21.13. Found: C, 59.14; H, 4.24; N, 4.55; S, 21.22.

5-Methyl-2-(2-phenylethyl)-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3g): a yellow solid; mp 118–120 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1332, 1167 cm$^{-1}$; $^1$H NMR δ 2.55 (s, 3H), 3.20–3.23 (m, 2H), 4.27–4.31 (m, 2H), 7.24–7.28 (m, 1H), 7.33–7.36 (m, 4H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 8.07 (s, 1H); $^{13}$C NMR δ 21.9, 33.5, 43.8, 120.2, 126.9, 127.1, 128.7 (2 overlapped Cs), 128.9, 130.8, 134.7, 137.5, 145.9, 185.5. HR-MS (positive). Caled for C$_{16}$H$_{16}$NO$_2$S$_2$ (M+H): 318.0622. Found: m/z 318.0612. Anal. Caled for C$_{16}$H$_{15}$NO$_2$S$_2$: C, 60.54; H, 4.76, N, 4.41; S, 20.20. Found: C, 60.67; H, 4.79, N, 4.52; S, 19.91.

2-(2-Methoxyethyl)-5-methyl-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3h): a yellow needles; mp 74–75 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1345, 1181 cm$^{-1}$; $^1$H NMR δ 2.55 (s, 3H), 3.41 (s, 3H), 3.81 (t, $J = 6.3$ Hz, 2H), 4.31 (t, $J = 6.3$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 8.06 (s, 1H); $^{13}$C NMR δ 21.9, 41.7, 59.0, 68.1, 120.2, 127.2, 128.5, 130.7, 134.7, 145.8, 186.3. HR-MS (positive). Caled for C$_{11}$H$_{14}$NO$_2$S$_2$ (M+H): 272.0415. Found: m/z 272.0410. Anal. Caled for C$_{11}$H$_{15}$NO$_3$S$_2$: C, 48.69; H, 4.83; N, 5.16. Found: C, 48.65; H, 4.79; N, 5.14.

(E)-N-Methyl-2-phenyl-1,2-benzothiazol-3-imine 1,1-Dioxide (3i): a pale-yellow solid; mp 117–119 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1677, 1320 cm$^{-1}$; $^1$H NMR δ 2.52 (s, 3H), 2.87 (s, 3H), 7.44–7.54 (m, 6H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.89 (s, 1H); $^{13}$C NMR δ 21.8, 37.6, 120.7, 123.9, 129.2, 129.4, 129.7, 131.4,

5-Chloro-2-ethyl-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3j): a yellow solid; mp 115–117 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1340, 1189 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 1.46 (t, \( J = 7.4 \) Hz, 3H), 4.16 (q, \( J = 7.4 \) Hz, 2H), 7.76 (s, 2H), 8.19 (s, 1H); \(^{13}\)C NMR \( \delta \) 12.6, 38.2, 121.6, 126.8, 129.5, 132.0, 133.9, 141.2, 183.2. HR-MS (negative). Calcd for \( \text{C}_9\text{H}_8\text{ClNO}_2\text{S}_2 \) (M): 260.9685. Found: \( m/z \) 260.9693. Anal. Calcd for \( \text{C}_9\text{H}_8\text{ClNO}_2\text{S}_2 \): C, 41.30; H, 3.08; N, 5.35. Found: C, 41.32; H, 2.97; N, 5.29.

5-Methoxy-2-methyl-1,2-benzothiazole-3(2H)-thione 1,1-Dioxide (3k): a yellow solid; mp 137–139 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1329, 1190 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 3.52 (s, 3H), 3.97 (s, 3H), 7.29 (dd, \( J = 8.6, 2.3 \) Hz, 1H), 7.69 (d, \( J = 2.3 \) Hz, 1H), 7.75 (d, \( J = 8.6 \) Hz, 1H); \(^{13}\)C NMR \( \delta \) 27.8, 56.3, 109.9, 121.0, 122.0, 123.0, 133.2, 164.5, 185.6. HR-MS (positive). Calcd for \( \text{C}_9\text{H}_{10}\text{NO}_3\text{S} \) (M): 244.0102. Found: \( m/z \) 244.0092. Anal. Calcd for \( \text{C}_9\text{H}_{10}\text{NO}_3\text{S} \): C, 44.43; H, 3.73; N, 5.76; S, 26.35. Found: C, 44.40; H, 3.58; N, 5.69; S, 26.74.

5-Methoxy-2-(E)-N-dimethyl-1,2-benzothiazol-3-imine 1,1-Dioxide (3k’): a yellow solid; mp 197–199 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1670, 1290 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 1.02 (t, \( J = 7.4 \) Hz, 3H), 2.94–2.99 (m, 2H), 4.67 (br s, 1H), 7.54 (dd, \( J = 8.0, 7.4 \) Hz, 1H), 7.60 (d, \( J = 8.6 \) Hz, 1H); \(^{13}\)C NMR \( \delta \) 24.5, 37.3, 56.1, 113.4, 116.6, 123.4, 127.9, 128.7, 145.1, 163.4. HR-MS (positive). Calcd for \( \text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_3\text{S} \) (M+H): 241.0647. Found: \( m/z \) 241.0639. Anal. Calcd for \( \text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_3\text{S} \): C, 49.99; H, 5.03; N, 11.66; S, 13.43. Found: C, 49.63; H, 4.97; N, 11.46; S, 13.43.

\( \text{N-Ethynaphthalene-1-sulfonamide (4b).} \) This compound was prepared from naphthalene-1-sulfonamide (\( 4b \)) and \( \text{EtNH}_2 \) according to the procedure described for the synthesis of \( 4a \).\(^\text{10} \) A white solid; mp 84–86 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 3271, 1311, 1176 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 1.02 (t, \( J = 7.4 \) Hz, 3H), 2.94–2.99 (m, 2H), 4.67 (br s, 1H), 7.54 (dd, \( J = 8.0, 7.4 \) Hz, 1H), 7.60 (d, \( J = 8.0 \) Hz, 1H), 7.67 (t, \( J = 7.4 \) Hz, 1H), 7.95 (d, \( J = 8.0 \) Hz, 1H), 8.07 (d, \( J = 8.0 \) Hz, 1H), 8.27 (d, \( J = 7.4 \) Hz, 1H), 8.66 (d, \( J = 8.0 \) Hz, 1H); \(^{13}\)C NMR \( \delta \) 15.1, 38.3, 124.1, 124.3, 126.8, 128.2, 128.3, 129.1, 129.7, 134.2, 134.3, 134.6. Anal. Calcd for \( \text{C}_{12}\text{H}_{13}\text{NO}_2\text{S} \): C, 61.25; H, 5.57; N, 5.95; S, 13.63. Found: C, 61.24; H, 5.62; N, 5.96; S, 13.61.

\textbf{Typical Procedure for the Preparation of Naphtho[2,1-\textit{d}] [1,2]thiazole-3(2H)-thione 1,1-Dioxides (5a) and (5b).} 2-Methynaphtho[2,1-\textit{d}] [1,2]thiazole-3(2H)-thione 1,1-Dioxide (5a). To a stirred solution of \( 4a \) (1.1 g, 5.1 mmol) in \( \text{THF} \) (30 mL) at 0 °C was added \( \text{n-BuLi} \) (1.6 M in hexane, 10 mmol). After 30 min, a solution of MeNCS (0.38 g, 5.1 mmol) in \( \text{THF} \) (3 mL) was added and stirring was continued for an additional 20 min before addition of saturated aqueous \( \text{NH}_4\text{Cl} \) (30 mL). The mixture was extracted with \( \text{AcOEt} \) (3×30 mL) and the combined extracts were washed with brine (30 mL) and dried...
Evaporation of the solvent gave a residual solid, which was recrystallized to give $5a$ (0.86 g, 63%); an orange solid; mp 180–182 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1331, 1179 cm$^{-1}$; $^1$H NMR δ 3.61 (s, 3H), 7.59 (ddd, $J = 8.0, 7.4, 1.1$ Hz, 1H), 7.82 (ddd, $J = 8.0, 7.4, 1.1$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 8.18 (d, $J = 8.6$ Hz, 1H), 8.23 (d, $J = 8.6$ Hz, 1H), 8.33 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR δ 27.7, 121.0, 123.6, 124.1, 127.2, 128.6, 129.1, 129.7, 130.2, 134.8, 135.7, 185.9. HR-MS (positive). Calcd for C$_{12}$H$_9$NO$_2$S$_2$ (M+H): 264.0153. Found: $m/z$ 264.0147. Anal. Calcd for C$_{12}$H$_9$NO$_2$S$_2$: C, 54.73; H, 3.45; N, 5.32; S, 24.35. Found: C, 54.78; H, 3.40; N, 5.47; S, 24.17.

2-Ethylnaphtho[2,1-d][1,2]thiazole-3(2H)-thione 1,1-Dioxide (5b): a yellow solid; mp 151–152 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1329, 1186 cm$^{-1}$; $^1$H NMR δ 1.55 (t, $J = 7.4$ Hz, 3H), 4.27 (q, $J = 7.4$ Hz, 2H), 7.75 (t, $J = 7.4$ Hz, 1H), 7.81 (t, $J = 7.4$ Hz, 1H), 8.02 (d, $J = 7.4$ Hz, 1H), 8.17 (d, $J = 8.6$ Hz, 1H), 8.23 (d, $J = 8.6$ Hz, 1H); $^{13}$C NMR δ 12.9, 38.0, 121.1, 123.7, 124.2, 127.4, 128.7, 129.1, 129.7, 130.1, 134.7, 135.8, 185.3. HR-MS (positive). Calcd for C$_{13}$H$_{12}$NO$_2$S$_2$ (M+H): 278.0309. Found: $m/z$ 278.0304. Anal. Calcd for C$_{13}$H$_{12}$NO$_2$S$_2$: C, 56.30; H, 4.00; N, 5.05; S, 23.12. Found: C, 56.35; H, 4.01; N, 5.15; S, 22.95.

2-Phenylnaphtho[2,1-d][1,2]thiazole-3(2H)-thione 1,1-Dioxide (5c). Compound (5c) was treated with $n$-BuLi and MeNCS and worked up as described for the preparation of 5a. The crude mixture was purified by column chromatography on SiO$_2$ (AcOEt/hexane 1:3) to afford 5c. An orange solid; mp 208–210 °C (hexane/CH$_2$Cl$_2$); IR (KBr) 1339, 1177 cm$^{-1}$; $^1$H NMR δ 7.57–7.64 (m, 5H), 7.79 (td, $J = 7.4, 1.1$ Hz, 1H), 7.84 (td, $J = 7.4, 1.1$ Hz, 1H), 8.07 (d, $J = 7.4$ Hz, 1H), 8.23 (d, $J = 8.6$ Hz, 1H), 8.32 (d, $J = 7.4$ Hz, 1H); $^{13}$C NMR δ 121.5, 123.8, 124.5, 127.2, 128.4, 129.2, 129.9, 130.0, 130.1, 130.2, 130.7, 134.7, 136.1, 186.9. HR-MS (positive). Calcd for C$_{17}$H$_{12}$NO$_2$S$_2$ (M+H): 326.0309. Found: $m/z$ 326.0298. Anal. Calcd for C$_{17}$H$_{11}$NO$_2$S$_2$: C, 62.75; H, 3.41; N, 4.30; S, 19.70. Found: C, 62.76; H, 3.36; N, 4.27; S, 20.07.

2-Methylnaphtho[1,2-d][1,2]thiazole-3(2H)-thione 1,1-Dioxide (8a) and 2-Methylnaphtho[2,3-d][1,2]thiazole-3(2H)-thione 1,1-Dioxide (8b). Compound (6) (0.28 g, 1.3 mmol) in THF (10 mL) was treated with $n$-BuLi (1.6 M in hexane; 2.6 mmol) and MeNCS (93 mg, 1.3 mmol) and worked up as described for the preparation of 5a. The crude product was dissolved in toluene (15 mL) and DBU (20 mg, 0.13 mmol) was added. After the solution was heated at reflux temperature for 8 h, the resulting mixture was worked up as described for the preparation of 3a. The residue was purified by column chromatography on SiO$_2$ to give an inseparable mixture of 8a and 8b (0.11 g, 32%; ca. 4:1 mixture): a yellow solid; IR (KBr) 1327, 1153 cm$^{-1}$; $^1$H NMR δ 3.53 (s, 2.4H), 3.59 (s, 0.6H), 7.70 (t, $J = Hz$, 0.8 H), 7.74–7.77 (m, 0.4H), 7.82 (t, $J = 7.4$ Hz, 0.8H), 7.85 (d, $J = 7.4$ Hz, 0.8H), 7.98 (d, $J = 7.4$ Hz, 0.8H), 8.04 (dd, $J = 8.6, 2.3$ Hz, 0.2H), 8.10 (dd, $J = 8.0, 2.3$ Hz, 0.2H), 8.28 (d, $J = 8.6$ Hz, 0.8H), 8.33 (s, 0.2H), 8.74 (s, 0.2H), 10.20 (d, $J = 8.6$ Hz, 0.8H); $^{13}$C NMR δ 27.6, 27.8, 115.0, 121.9, 123.9, 126.6, 127.1,
128.0, 128.3, 129.0, 129.2, 129.3, 129.5, 130.0, 130.1, 130.4, 131.1, 131.6, 134.4, 135.1, 136.2, 136.8, 185.9, 186.4. HR-MS (positive). Calcd for C_{12}H_{10}NO_{2}S_{2} (M+H): 264.0153. Found: m/z 264.0147. Anal. Calcd for C_{12}H_{9}NO_{2}S_{2}: C, 54.73; H, 3.45; N, 5.32. Found: C, 54.71; H, 3.49, N, 5.33.

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REFERENCES AND NOTES