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

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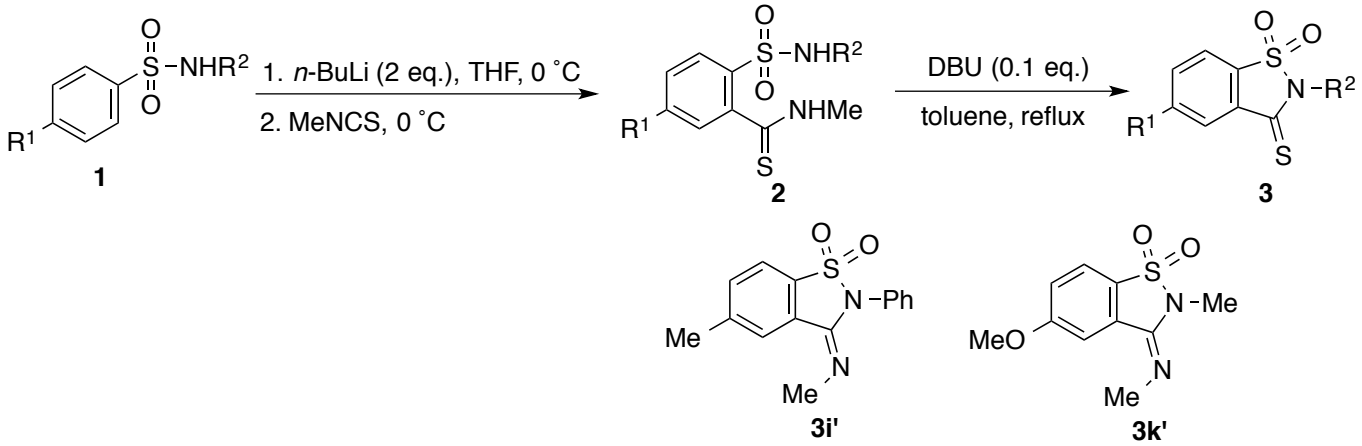
Abstract – An efficient method for the preparation of 2-alkyl-1,2-benzothiazole-3(2*H*)-thione 1,1-dioxides has been developed. Thus, the reaction of 2,*N*-dilithio derivatives of *N*-alkylbenzenesulfonamides with methyl isothiocyanate affords 2-[(alkylamino)sulfonyl]-*N*-methylbenzothioamides, which 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(2*H*)-thione 1,1-dioxide structure (thiosaccharin) have been reported to be versatile as agricultural or horticultural plant disease control agents or pesticides.[1] Thiocarbonylation of the carbonyl function of 1,2-benzothiazol-3(2*H*)-one 1,1-dioxides (saccharins) with awkward sulfurization agents, such as P_2S_5 and Lawesson's reagent, has traditionally been used for the synthesis of this type of heterocycles.[2] 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,[3] we have recently reported that 1,2-benzothiazol-3(2*H*)-imine 1,1-dioxide[4] and 4*H*-1,3,2-benzodithiazin-4-imine 1,1-dioxide derivatives[5] can be obtained on exposure of 2-(aminosulfonyl)benzothioamides, derived from the reaction of 2,*N*-dilithiobenzenesulfonamides[6] 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(2*H*)-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

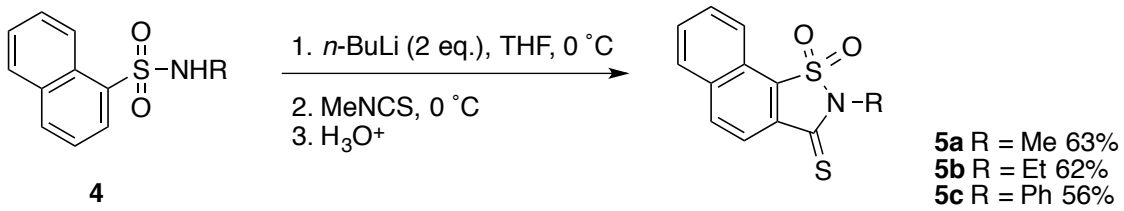
Table 1. Preparation of 2*H*-1,2-benzothiazole-3(2*H*)-thione 1,1-dioxides (**3**)

Entry	**1**	R^1	R^2	**2**	Yield/%[a]	**3**	Yield/%[a]
1	**1a**	H	Me	**2a**	58[b]	**3a**	72
2	**1b**	Me	Me	**2b**	71	**3b**	85
3	**1c**	Me	*n*-Bu	**2c**	60[b]	**3c**	73
4	**1d**	Me	*i*-Bu	**2d**	66	**3d**	63
5	**1e**	Me	CH_2=$CHCH_2$	**2e**	61	**3e**	85
6	**1f**	Me	Bn	**2f**	40	**3f**	77
7	**1g**	Me	$Ph(CH_2)_2$	**2g**	62	**3g**	93
8	**1h**	Me	$MeO(CH_2)_2$	**2h**	63	**3h**	73
9	**1i**	Me	Ph	**2i**	36	**3i**	0[c]
10	**1j**	Cl	Et	**2j**	51(30[b])	**3j**	87
11	**1k**	OMe	Me	**2k**	83	**3k**	53[d]

[a] Yields of isolate products. [b] See ref. 5. [c] Compound **3i'** was obtained in 32% yield. [d] Compound **3k'** was obtained in 10% yield.

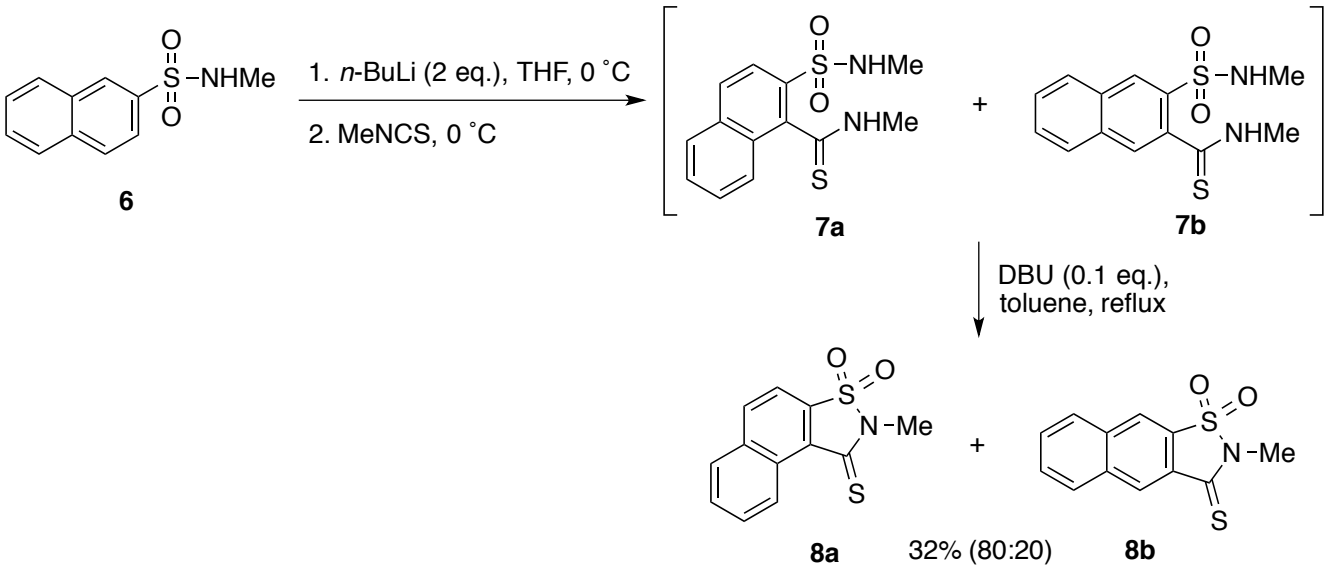
The preparation of benzothiazolethione 1,1-dioxides (**3**) was carried out as illustrated in Scheme 1. As the first step of the present sequence, *N*-substituted benzenesulfonamides (**1**) were treated with two equivalents of butyllithium in THF at 0 ˚C and the resulting 2,*N*-dilithio products were 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,(*E*)-*N*-dimethyl-2-phenyl-1,2-benzothiazol-3(2*H*)-imine 1,1-dioxide (**3i'**)[4] 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(2*H*)-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.



Scheme 2

Subsequently, the preparation of 2-substituted naphtho[2,1-*d*][1,2]thiazole-3(2*H*)-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 dilithiated 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.



Scheme 3

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(2*H*)-one 1,1-dioxide (**8a**) and 2-methylnaphtho[2,3-*d*][1,2]thiazol-3(2*H*)-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(2*H*)-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. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ 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 PF_{254}. 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**),[7] (**1g**),[8] (**1k**),[9] *N*-substituted 2-[(methylamino)sulfonyl]benzothioamides (**2a**),[4] (**2c**),[4] (**2j**),[4] and *N*-substituted naphthalene-1-sulfonamides (**4a**),[10] (**4c**)[11] 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**.[4]

5,*N*-Dimethyl-2-[(methylamino)sulfonyl]benzothioamide (2b): a pale-yellow solid; mp 161–163 °C (hexane/CH_2Cl_2); IR (KBr) 3281, 3201, 1367, 1167 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{10}H_{14}N_2O_2S_2$: 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]sulfonyl]}benzothioamide (2d): a pale-yellow solid; mp 95–97 °C (hexane/CH_2Cl_2); 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); ^{13}C 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 $C_{13}H_{20}N_2O_2S_2$: 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]sulfonyl]}benzothioamide (2e): a pale-yellow solid; mp 96–98 °C (hexane/CH_2Cl_2); 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); ^{13}C NMR δ 21.3, 33.2, 46.0, 117.7, 128.8, 129.3, 129.5, 131.5, 132.7, 141.3, 144.2, 199.2. Anal. Calcd for $C_{12}H_{16}N_2O_2S_2$: 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]sulfonyl]}benzothioamide (2f): a yellow solid; mp 133–135 °C (hexane/CH_2Cl_2); 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); ^{13}C 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 $C_{16}H_{18}N_2O_2S_2$: 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]sulfonyl]}benzothioamide (2g): a pale-yellow solid; mp 130–133 °C (hexane/CH_2Cl_2); 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); ^{13}C 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 $C_{17}H_{20}N_2O_2S_2$: 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]sulfonyl]}-5,*N*-dimethylbenzothioamide (2h): a pale-yellow solid; mp 138–140 °C (hexane/CH_2Cl_2); 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); ^{13}C 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 $C_{12}H_{18}N_2O_3S_2$: 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)sulfonyl]benzothioamide (2i): a yellow solid; mp 163–164 °C

(hexane/CH_2Cl_2); 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); ^{13}C 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 $C_{15}H_{16}N_2O_2S_2$: 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/CH_2Cl_2); 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); ^{13}C 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 $C_{10}H_{14}N_2O_3S_2$: 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(2*H*)-thione 1,1-Dioxides (3). 2-Methyl-1,2-benzothiazole-3(2*H*)-thione 1,1-Dioxide (3a).[12] 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 (Na_2SO_4) and concentrated by evaporation. The residual solid was recrystallized to afford **3a** (0.15 g, 72%); a yellow solid; mp 174–176 ˚C (hexane/CH_2Cl_2) (lit.,[13] 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); ^{13}C 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(2*H*)-thione 1,1-Dioxide (3b): a yellow solid; mp 154–156 ˚C (hexane/CH_2Cl_2); IR (KBr) 1332, 1189 cm^{-1}; ^1H NMR δ 2.55 (s, 3H), 3.52 (s, 3H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 8.06 (s, 1H); ^{13}C NMR δ 21.9, 27.6, 120.2, 127.0, 128.6, 130.9, 134.6, 145.8, 186.0. HR-MS (positive). Calcd for $C_9H_{10}NO_2S_2$ (M+H): 228.0153. Found: *m*/*z* 228.0148. Anal. Calcd for $C_9H_9NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (3c): a yellow oil; R_f 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); ^{13}C 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 $C_{12}H_{16}NO_2S_2$ (M+H): 270.0622. Found: *m*/*z* 270.0617. Anal. Calcd for $C_{12}H_{15}NO_2S_2$: C, 53.51; H, 5.61; N, 5.20; S, 23.80. Found: C, 53.58; H, 5.85; N, 5.20; S, 23.93.

5-Methyl-2-(2-methylpropyl)-1,2-benzothiazole-3(2*H*)-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). Calcd for $C_{12}H_{16}NO_2S_2$ (M+H): 270.0622. Found: *m*/*z* 270.0617. Anal. Calcd for $C_{12}H_{15}NO_2S_2$: 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(2*H*)-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). Calcd for $C_{11}H_{12}NO_2S_2$ (M+H): 254.0309. Found: *m*/*z* 254.0304. Anal. Calcd for $C_{11}H_{11}NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (3f): a yellow solid; mp 137–139 °C (hexane/CH_2Cl_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). Calcd for $C_{15}H_{14}NO_2S_2$ (M+H): 304.0466. Found: *m*/*z* 304.0459. Anal. Calcd for $C_{15}H_{13}NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (3g): a yellow solid; mp 118–120 °C (hexane/CH_2Cl_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). Calcd for $C_{16}H_{16}NO_2S_2$ (M+H): 318.0622. Found: *m*/*z* 318.0612. Anal. Calcd for $C_{16}H_{15}NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (3h): a yellow needles; mp 74–75 °C (hexane/CH_2Cl_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). Calcd for $C_{11}H_{14}NO_3S_2$ (M+H): 272.0415. Found: *m*/*z* 272.0410. Anal. Calcd for $C_{11}H_{13}NO_3S_2$: 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_2Cl_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,

132.0, 133.2, 133.3, 141.1, 145.1. HR-MS (positive). Calcd for $C_{15}H_{15}N_2O_2S$ (M+H): 287.0854. Found: *m*/*z* 287.0846. Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.78; S, 11.20. Found: C, 62.93; H, 4.88; N, 9.65; S, 11.04.

5-Chloro-2-ethyl-1,2-benzothiazole-3(2*H*)-thione 1,1-Dioxide (3j): a yellow solid; mp 115–117 ˚C (hexane/CH_2Cl_2); IR (KBr) 1340, 1189 cm^{-1}; ^1H NMR δ 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 δ 12.6, 38.2, 121,6, 126.8, 129.5, 132.0, 133.9, 141.2, 183.2. HR-MS (negative). Calcd for $C_9H_8ClNO_2S_2$ (M): 260.9685. Found: *m*/*z* 260.9693. Anal. Calcd for $C_9H_8ClNO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (3k): a yellow solid; mp 137–139 ˚C (hexane/CH_2Cl_2); IR (KBr) 1329, 1190 cm^{-1}; ^1H NMR δ 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 δ 27.8, 56.3, 109.9, 121.0, 122.0, 123.0, 133.2, 164.5, 185.6. HR-MS (positive). Calcd for $C_9H_{10}NO_3S$ (M): 244.0102. Found: *m*/*z* 244.0092. Anal. Calcd for $C_9H_9NO_3S_2$: 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/CH_2Cl_2); IR (KBr) 1670, 1298 cm^{-1}; ^1H NMR δ 3.12 (s, 3H), 3.66 (s, 3H), 3.93 (s, 3H), 7.21 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.60 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 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 $C_{10}H_{13}N_2O_3S$ (M+H): 241.0647. Found: *m*/*z* 241.0639. Anal. Calcd for $C_{10}H_{12}N_2O_3S$: C, 49.99; H, 5.03; N, 11.66; S, 13.34. Found: C, 49.63; H, 4.97; N, 11.46; S, 13.43.

***N*-Ethylnaphthalene-1-sulfonamide (4b).** This compound was prepared from naphthalene-1-sulfonamide (**4b**) and $EtNH_2$ according to the procedure described for the synthesis of **4a**.[10] A white solid; mp 84–86 ˚C (hexane/CH_2Cl_2); IR (KBr) 3271, 1311, 1176 cm^{-1}; ^1H NMR δ 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 (dd, *J* = 8.0, 7.4 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 δ 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 $C_{12}H_{13}NO_2S$: 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.

Typical Procedure for the Preparation of Naphtho[2,1-*d*][1,2]thiazole-3(2*H*)-thione 1,1-Dioxides (5a) and (5b). 2-Methylnaphtho[2,1-*d*][1,2]thiazole-3(2*H*)-thione 1,1-Dioxide (5a). To a stirred solution of **4a** (1.1 g, 5.1 mmol) in THF (30 mL) at 0 ˚C was added *n*-BuLi (1.6 M in hexane, 10 mmol). After 30 min, a solution of MeNCS (0.38 g, 5.1 mmol) in THF (3 mL) was added and stirring was continued for an additional 20 min before addition of saturated aqueous NH_4Cl (30 mL). The mixture was extracted with AcOEt (3 × 30 mL) and the combined extracts were washed with brine (30 mL) and dried

(Na_2SO_4). 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_2Cl_2); IR (KBr) 1331, 1179 cm^{-1}; ^1H 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 $C_{12}H_{10}NO_2S_2$ (M+H): 264.0153. Found: *m*/*z* 264.0147. Anal. Calcd for $C_{12}H_9NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (5b): a yellow solid; mp 151–152 °C (hexane/CH_2Cl_2); IR (KBr) 1329, 1186 cm^{-1}; ^1H 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), 8.32 (d, *J* = 7.4 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 $C_{13}H_{12}NO_2S_2$ (M+H): 278.0309. Found: *m*/*z* 278.0304. Anal. Calcd for $C_{13}H_{11}NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (5c). Compound (**4c**) 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_2Cl_2); IR (KBr) 1339, 1177 cm^{-1}; ^1H 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* = 8.6 Hz, 1H), 8.39 (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, 130.8, 134.7, 136.1, 186.9. HR-MS (positive). Calcd for $C_{17}H_{12}NO_2S_2$ (M+H): 326.0309. Found: *m*/*z* 326.0298. Anal. Calcd for $C_{17}H_{11}NO_2S_2$: 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(2*H*)-thione 1,1-Dioxide (8a) and 2-Methylnaphtho[2,3-*d*][1,2]thiazole-3(2*H*)-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}; ^1H 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 $C_{12}H_{10}NO_2S_2$ (M+H): 264.0153. Found: *m/z* 264.0147.Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 54.73; H, 3.45; N, 5.32. Found: C, 54.71; H, 3.49, N, 5.33.

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