HETEROCYCLES, Vol. 96, No. 9, 2018, pp. 1570 - 1582. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 11th July, 2018, Accepted, 1st August, 2018, Published online, 10th August, 2018
DOI: 10.3987/COM-18-13959

AN EFFICIENT SYNTHESIS OF 4-MONO- and 4,4-DI-SUBSTITUTED 3,4-DIHYDRO-2*H*-1-BENZOTHIOPYRAN 1,1-DIOXIDES BY LDA-MEDIATED CYCLIZATION OF *o*-(METHYLSULFONYL)STYRENES

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Abstract – A new and efficient method for the preparation of 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxide derivatives has been developed. α-Substituted *o*-(methylsulfonyl)styrenes, which can be derived from α-substituted *o*-bromostyrenes by an easily operated two-step sequence, are cyclized on treatment with lithium diisopropylamide (LDA) to give, after aqueous workup, the corresponding 4-monosubstituted 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxides. Addition of electrophiles prior to aqueous workup provides 4,4-disubstituted derivatives.

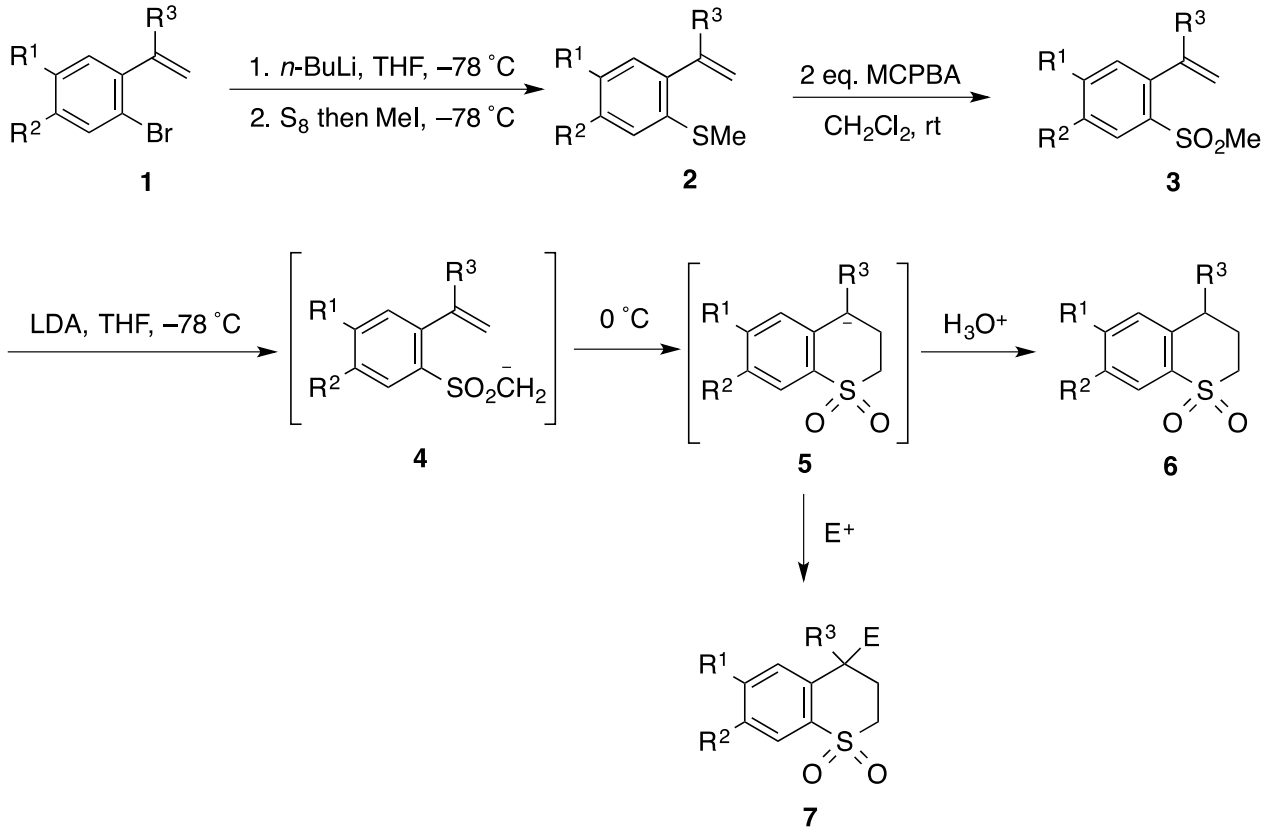
INTRODUCTION

Molecules with the 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxide skeleton have attracted much attention because of their biological, such as cathepsin L inhibitory[1d] and α_{1D} adrenoceptor antagonistic,[1e] activities.[1] The oxidation of the respective 3,4-dihydro-2*H*-1-benzothiopyrans with appropriate oxidants, such as peracetic acid[1d] and oxone,[2] is most commonly utilized for the preparation of these derivatives, though an elegant preparation of 2,3,4-triaryl derivatives by the Pd-catalyzed α-arylation of an (*o*-alkenylated phenyl) methyl sulfone prepared utilizing the Rh-catalyzed *o*-alkenylation of phenyl sulfones with alkynes and subsequent cyclization with lithium *tert*-butoxide has recently been developed by Satoh and Miura.[3] In this paper we wish to report a convenient and unprecedented route for the preparation of 4-mono- (**6**) and 4,4-di-substituted 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxide

derivatives (**7**) by LDA-mediated cyclization of the respective α-substituted *o*-(methylsulfonyl)styrenes (**3**), which can be prepared from readily available α-substituted *o*-bromostyrenes (**1**) utilizing an easily operated two-step sequence.

RESULTS AND DISCUSSION

The preparation of 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxide derivatives (**6**) and (**7**) from compounds (**1**) was conducted according to the procedure illustrated in Scheme 1. The starting materials (**1**) were easily accessible by the literature methods (see Experimental) and were treated with butyllithium in THF at –78 ˚C to generate the corresponding α-substituted *o*-lithiostyrenes, which were then allowed to react successively with sulfur and methyl iodide to give α-substituted *o*-(methylsulfanyl)styrenes (**2**), *via* generation of the corresponding *o*-vinylbenzenethiolates, in moderate to good yields. Oxidation of these methyl sulfides (**2**) with two equivalents of *m*-chloroperbenzoic acid (MCPBA) afforded α-substituted *o*-(methylsulfonyl)styrenes (**3**) in moderate to fair yields.



Scheme 1

The cyclization of **3** to 4-substituted 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxides (**6**) was easily achieved on treatment with LDA in THF at –78 ˚C and the subsequent warming the reaction mixture to 0

˚C. During this warming, the color of the reaction mixtures changed from yellow to dark red. This indicated the initially formed carbanions α to the sulfonyl group [intermediate (**4**)] attacked on the β-carbon of the styrene moiety to generate the benzylic anions (**5**). After aqueous workup the desired products (**6**) could be easily isolated in generally good yields, as listed in Table 1, using column chromatography on silica gel. The lowering of the yields of the products (**6f**) (Entry 6, R^3 = 4-$MeOC_6H_4$), (**6i**) (Entry 9, R^2 = OMe), and (**6j**) (Entry 10, R^3 = Me) may suggest the less stability of the corresponding intermediate benzylic anions (**5**) compared to the others.

Table 1. Preparation of 4-substituted 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxides (**6**)

Entry	**1**	R^1	R^2	R^3	**2**	Yield/%[a]	**3**	Yield/%[a]	Temp	**6**	Yield/%[a]
1	**1a**	H	H	Ph	**2a**	58	**3a**	55	0 ˚C	**6a**	73
2	**1b**	H	H	*m*-Tol	**2b**	70	**3b**	66	0 ˚C	**6b**	60
3	**1c**	H	H	*p*-Tol	**2c**	75	**3c**	64	0 ˚C	**6c**	62
4	**1d**	H	H	3-ClC_6H_4	**2d**	71	**3d**	71	0 ˚C	**6d**	82
5	**1e**	H	H	4-ClC_6H_4	**2e**	86	**3e**	59	0 ˚C	**6e**	70
6	**1f**	H	H	4-$MeOC_6H_4$	**2f**	91	**3f**	47	0 ˚C	**6f**	46
7	**1g**	OMe	H	Ph	**2g**	75	**3g**	75	0 ˚C	**6g**	70
8	**1h**	OMe	H	4-ClC_6H_4	**2h**	68	**3h**	74	0 ˚C	**6h**	81
9	**1i**	OMe	OMe	Ph	**2i**	76	**3i**	60	0 ˚C	**6i**	44
10	**1j**	H	H	Me	**2j**	76	**3j**	76	rt	**6j**	25

[a] Yields of isolated products.

Table 2. Preparation of 4-alkyl-4-aryl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxides (**7**)

Entry	**3**	R^1	R^2	R^3	E^+	E	**7**	Yield/%[a]
1	**3a**	H	H	Ph	MeI	Me	**7a-i**	79
2	**3a**	H	H	Ph	BnBr	Bn	**7a-ii**	78
3	**3a**	H	H	Ph	MeSSMe	MeS	**7a-iii**	70
4	**3b**	H	H	*m*-Tol	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$	**7b**	72
5	**3d**	H	H	3-ClC_6H_4	BnBr	Bn	**7d**	83
6	**3g**	OMe	H	Ph	CH_2=$CHCH_2Br$	CH_2=$CHCH_2$	**7g**	82
7	**3h**	OMe	H	4-ClC_6H_4	MeI	Me	**7h**	77

[a] Yields of isolated products.

Next, introduction of substituents at the 4-position of the products was examined in order to obtain 4,4-disubstituted 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxides (**7**). It could be performed by simply adding electrophiles to the reaction mixtures resulting from the reactions of **3** with LDA as described above before aqueous workup to afford the desired products in the yields summarized in Table 2. As can be seen from it, this protocol was equally effective for not only activated haloalkanes, such as methyl iodide, allyl bromide and benzyl bromide, but also dimethyl disulfide giving the corresponding methylsulfanylated product (**7a-iii**) in good yield (Entry 3). Unfortunately, however, the use of 2-bromoacetonitrile resulted in the formation of a complicated mixture of the products, from which no

more than trace amount of the expected product could be isolated. This may be attributed that the proton transfer from 2-bromoacetonitrlie to benzyl anion intermediate (**5**) occurred before cyanomethylation and the resulting lithiated 2-bromoacetonitrile caused the complexation of the products. To the best of our knowledge, there has been the only example of preparing 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxide carrying an alkyl and an aryl substituent at the 4-position.[4]

In summary, we have developed a simple procedure for the synthesis of 3,4-dihydro-2*H*-1-benzothiopyran 1,1-dioxides utilizing LDA-mediated cyclization of α-substituted *o*-(methylsulfonyl)styrenes, of which preparation is based on the generation of *o*-vinylbenzenethiolate intermediates from α-substituted *o*-bromostyrenes. The present method may be of use in organic synthesis due to its operational simplicity and the ready availability of the starting materials. We are currently investigating the further utilization of these intermediates for the construction of sulfur containing heterocycles and will report on our finding shortly.

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 or ESI, positive) spectrometer. 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. 2-Bromo-1-(ethenyl)benzenes (**1a**),[5] (**1b**),[6] (**1c**),[7] (**1d**),[8] (**1e**),[9] (**1f**),[10] (**1g**),[9] (**1h**),[7] (**1i**),[11] and (**1j**)[12] were prepared according to the appropriate reported procedures. *n*-BuLi was supplied by Asia Lithium Corporation. All other chemicals used in this study were commercially available.

Typical Procedure for the Preparation of Sulfides (2). 1-(Methylsulfanyl)-2-(1-phenylethenyl)benzene (2a). To a stirred solution of **1a** (0.84 g, 3.3 mmol) in THF (5 mL) at –78 ˚C was added *n*-BuLi (1.6 M in hexane, 3.3 mmol) dropwise. After 15 min, a solution of S_8 (0.10 g, 3.3 mmol) in THF (15 mL) was added dropwise, then the mixture was treated with MeI (0.46 g, 3.3 mmol) at the same temperature. After 20 min, saturated aqueous NH_4Cl (30 mL) was added and the mixture was extracted with AcOEt (3 × 20 mL). The combined extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 to afford **2a** (0.43 g, 58%); a colorless oil; R_f 0.31 (CH_2Cl_2/hexane 1:12); IR (neat) 1614 cm^{-1}; ^{1}H NMR δ 2.33 (s, 3H), 5.28 (s, 1H), 5.83 (s, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.20–7.29 (m, 7H), 7.33 (t, J = 7.4 Hz, 1H); ^{13}C NMR

δ 15.9, 116.1, 124.6, 125.2, 126.6, 127.7, 128.1, 128.3, 130.2, 137.7, 139.9, 140.7, 148.1. HR-MS (DART). Calcd for $C_{15}H_{15}S$ (M+H): 227.0894. Found: *m*/*z* 227.0888.

1-[1-(3-Methylphenyl)ethenyl]-2-(methylsulfanyl)benzene (2b): a colorless oil; R_f 0.31 (CH_2Cl_2/hexane 1:6); IR (neat) 1616 cm^{-1}; ^1H NMR δ 2.32 (s, 3H), 2.34 (s, 3H), 5.26 (s, 1H), 5.82 (s, 1H), 7.08 (t, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 7.16–7.23 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 15.8, 21.5, 116.0, 123.8, 124.5, 124.9, 127.1, 128.07, 128.14, 128.5, 130.2, 137.6, 137.8, 139.8, 140.6, 148.1. HR-MS (DART). Calcd for $C_{16}H_{17}S$ (M+H): 241.1051. Found: *m*/*z* 241.1044.

1-[1-(4-Methylphenyl)ethenyl]-2-(methylsulfanyl)benzene (2c): a colorless oil; R_f 0.34 (CH_2Cl_2/hexane 1:5); IR (neat) 1613 cm^{-1}; ^1H NMR δ 2.33 (s, 3H), 2.34 (s, 3H), 5.23 (s, 1H), 5.64 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.15–7.24 (m, 5H), 7.33 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 15.8, 21.2, 115.2, 124.5, 124.8, 126.4, 129.0, 129.0, 130.2, 136.9, 137.56, 137.60, 140.6, 147.8. HR-MS (DART). Calcd for $C_{16}H_{17}S$ (M+H): 241.1051. Found: *m*/*z* 241.1046.

1-[1-(3-Chlorophenyl)ethenyl]-2-(methylsulfanyl)benzene (2d): a white solid; mp 43–47 ˚C (pentane); IR (KBr) 1615 cm^{-1}; ^1H NMR δ 2.35 (s, 3H), 5.33 (s, 1H), 5.83 (s, 1H), 7.15–7.36 (m, 8H); ^{13}C NMR δ 15.8, 117.4, 124.6, 124.8, 125.1, 126.6, 127.7, 128.4, 129.5, 130.2, 134.2, 137.6, 139.7, 141.8, 146.9. HR-MS (DART). Calcd for $C_{15}H_{14}ClS$ (M+H): 261.0504. Found: *m*/*z* 261.0498.

1-[1-(4-Chlorophenyl)ethenyl]-2-(methylsulfanyl)benzene (2e): a pale-yellow oil; R_f 0.31 (AcOEt/hexane 1:80); IR (KBr) 1614 cm^{-1}; ^1H NMR δ 2.34 (s, 3H), 5.29 (s, 1H), 5.80 (s, 1H), 7.19–7.34 (m, 8H); ^{13}C NMR δ 15.8, 116.6, 124.6, 125.1, 127.8, 128.35, 128.43, 130.2, 133.5, 137.6, 138.3, 140.0, 147.0. HR-MS (DART). Calcd for $C_{15}H_{14}ClS$ (M+H): 261.0504. Found: *m*/*z* 261.0492.

1-[1-(4-Methoxyphenyl)ethenyl]-2-(methylsulfanyl)benzene (2f): a white solid; mp 43–45 ˚C (pentane); IR (KBr) 1606 cm^{-1}; ^1H NMR δ 2.35 (s, 3H), 3.79 (s, 3H), 5.17 (s, 1H), 5.73 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.19–7.25 (m, 5H), 7.32 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR 15.8, 55.2, 113.6, 114.1, 124.5, 124.9, 127.7, 128.0, 130.1, 132.4, 137.6, 140.7, 147.4, 159.3. HR-MS (DART). Calcd for $C_{16}H_{17}OS$ (M+H): 257.1000. Found: *m*/*z* 257.0989.

4-Methoxy-1-(methylsulfanyl)-2-(1-phenylethenyl)benzene (2g): a colorless oil; R_f 0.35 (AcOEt/hexane 1:20); IR (neat) 1615 cm^{-1}; ^1H NMR δ 2.26 (s, 3H), 3.81 (s, 3H), 5.28 (s, 1H), 5.82 (d, *J* = 1.1 Hz, 1H), 6.83 (d, *J* = 2.9 Hz, 1H), 6.90 (dd, *J* = 8.6, 2.9 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.28–7.31 (m, 5H); ^{13}C NMR δ 17.6, 55.4, 113.9, 115.7, 116.1, 126.5, 127.7, 127.9, 128.2, 129.2, 139.8, 143.2, 148.3, 157.7. HR-MS (DART). Calcd for $C_{16}H_{17}OS$ (M+H): 257.1000. Found: *m*/*z* 257.0995.

2-[1-(4-Chlorophenyl)ethenyl]-4-methoxy-1-(methylsulfanyl)benzene (2h): a colorless oil; R_f 0.35 (AcOEt/hexane 1:20); IR (neat) 1611 cm^{-1}; ^1H NMR δ 2.25 (s, 3H), 3.80 (s, 3H), 5.27 (s, 1H), 5.78 (d, *J* = 1.1 Hz, 1H), 6.79 (d, *J* = 2.9 Hz, 1H), 6.90 (dd, *J* = 8.6 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6

Hz, 3H); ^{13}C NMR δ 17.6, 55.4, 114.0, 116.1, 116.2, 127.8, 127.8, 128.4, 129.4, 133.5, 128.4, 142.7, 147.3, 157.8. HR-MS (DART). Calcd for $C_{16}H_{16}ClOS$ (M+H): 291.0610. Found: *m*/*z* 291.0606.

1,2-Dimethoxy-4-(methylsulfanyl)-5-(1-phenylethenyl)benzene (2i): a pale-yellow oil; R_f 0.34 (AcOEt/hexane 1:7); IR (neat) 1614 cm^{-1}; ^{1}H NMR δ 2.28 (s, 3H), 3.85 (s, 3H), 3.93 (s, 3H), 5.26 (s, 1H), 5.81 (s, 1H), 6.77 (s, 1H), 6.90 (s, 1H), 7.25–7.30 (m, 5H); ^{13}C NMR δ 18.1, 56.06, 56.08, 112.4, 113.9, 115.7, 126.6, 127.6, 127.8, 128.2, 135.3, 140.4, 147.4, 148.2, 148.7. HR-MS (DART). Calcd for $C_{17}H_{19}O_2S$ (M+H): 287.1106. Found: *m*/*z* 287.1099.

1-(1-Methylethenyl)-2-(methylsulfanyl)benzene (2j):[13] a colorless oil; R_f 0.34 (CH_2Cl_2/hexane 1:30). The ^{1}H NMR data for this compound were identical to those reported previously.[14]

Typical Procedure for the Preparation of Sulfones (3). 1-(Methylsulfonyl)-2-(1-phenylethenyl)benzene (3a). A mixture of **2a** (0.43 g, 1.9 mmol) and MCPBA (containing 20% H_2O; 0.81 g, 3.8 mmol) in CH_2Cl_2 (10 mL) was stirred for 50 min at rt. The precipitate was filtered off under reduced pressure and the filtrate was diluted with CH_2Cl_2 (10 mL). The organic solution was washed with 5% aqueous $Na_2S_2O_3$ and 10% aqueous $NaHCO_3$ (10 mL each), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 to afford **3a** (0.27 g, 55%); a colorless amorphous powder; R_f 0.29 (Et_2O/hexane 7:10); IR (KBr) 1615, 1317, 1123 cm^{-1}; ^{1}H NMR δ 2.71 (s, 3H), 5.36 (s, 1H), 5.95 (s, 1H), 7.26–7.30 (m, 5H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.56 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 44.0, 116.9, 126.9, 128.1, 128.3, 128.4, 129.6, 132.7, 133.4, 139.0, 139.9, 141.4, 146.5. HR-MS (DART). Calcd for $C_{15}H_{15}O_2S$ (M+H): 259.0793. Found: *m*/*z* 259.0788.

1-[1-(3-Methylphenyl)ethenyl]-2-(methylsulfonyl)benzene (3b): a colorless gum; R_f 0.24 (Et_2O/hexane 3:4); IR (neat) 1621, 1311, 1151 cm^{-1}; ^{1}H NMR δ 2.32 (s, 3H), 2.72 (s, 3H), 5.34 (s, 1H), 5.94 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.12 (s, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.56 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.66 (td, *J* = 7.4, 1.1 Hz, 1H), 8.16 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR δ 21.5, 44.0, 116.8, 124.2, 127.4, 128.2, 128.3, 128.9, 129.5, 132.7, 133.3, 138.0, 138.9, 139.8, 141.5, 146.5. HR-MS (DART). Calcd for $C_{16}H_{17}O_2S$ (M+H): 273.0949. Found: *m*/*z* 273.0944.

1-[1-(4-Methylphenyl)ethenyl]-2-(methylsulfonyl)benzene (3c): a colorless gum; R_f 0.28 (Et_2O/hexane 3:5); IR (neat) 1615, 1306, 1148 cm^{-1}; ^{1}H NMR δ 2.33 (s, 3H), 2.75 (s, 3H), 5.30 (s, 1H), 5.93 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 8.16 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 21.1, 44.0, 116.1, 126.7, 128.3, 129.1, 129.5, 132.7, 133.3, 137.1, 138.0, 139.0, 141.6, 146.2. HR-MS (DART). Calcd for $C_{16}H_{17}O_2S$ (M+H): 273.0949. Found: *m*/*z* 273.0943.

1-[1-(3-Chlorophenyl)ethenyl]-2-(methylsulfonyl)benzene (3d): a colorless oil; R_f 0.26 (Et_2O/hexane 1:1); IR (neat) 1619, 1311, 1151 cm^{-1}; ^1H NMR δ 2.81 (s, 3H), 5.38 (s, 1H), 5.97 (s, 1H), 7.14 (ddd, *J* = 6.3, 2.3, 1.7 Hz, 1H), 7.24–7.27 (m, 3H), 7.38 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.60 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.69 (td, *J* = 7.4, 1.1 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 44.3, 117.8, 125.1, 126.7, 128.1, 128.7, 129.6, 129.8, 132.7, 133.6, 134.3, 138.9, 140.6, 141.7, 145.6. HR-MS (DART). Calcd for $C_{15}H_{14}ClO_2S$ (M+H): 293.0403. Found: *m*/*z* 293.0398.

1-[1-(4-Chlorophenyl)ethenyl]-2-(methylsulfonyl)benzene (3e): a colorless oil; R_f 0.30 (Et_2O/hexane 1:1); IR (neat) 1618, 1307, 1148 cm^{-1}; ^1H NMR δ 2.81 (s, 3H), 5.34 (s, 1H), 5.94 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 8.15 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 44.4, 117.0, 128.1, 128.5, 128.7, 129.7, 132.6, 133.5, 134.0, 138.4, 139.0, 140.9, 145.8. HR-MS (DART). Calcd for $C_{15}H_{14}ClO_2S$ (M+H): 293.0403. Found: *m*/*z* 293.0390.

1-[1-(4-Methoxyphenyl)ethenyl]-2-(methylsulfonyl)benzene (3f): a colorless gum; R_f 0.27 (Et_2O/hexane 4:5); IR (neat) 1607, 1321, 1148 cm^{-1}; ^1H NMR δ 2.77 (s, 3H), 3.79 (s, 3H), 5.24 (s, 1H), 5.86 (s, 1H), 6.83 (d, *J* = 9.2 Hz, 2H), 7.19 (d, *J* = 9.2 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.55 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 44.1, 55.2, 113.7, 114.1, 115.1, 128.1, 128.3, 129.5, 129.9, 132.1, 132.6, 133.3, 139.0, 141.7. HR-MS (DART). Calcd for $C_{16}H_{17}O_3S$ (M+H): 289.0898. Found: *m*/*z* 289.0886.

4-Methoxy-1-(methylsulfonyl)-2-(1-phenylethenyl)benzene (3g): a white solid; mp 125–128 ˚C (hexane/CH_2Cl_2); IR (neat) 1621, 1333, 1153 cm^{-1}; ^1H NMR δ 2.65 (s, 3H), 3.90 (s, 3H), 5.35 (s, 1H), 5.92 (s, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.28–7.33 (m, 5H), 8.07 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 44.2, 55.7, 112.9, 116.6, 118.1, 126.9, 128.1, 128.3, 130.8, 132.1, 139.7, 143.6, 146.6, 163.0. Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.48; H, 5.60; S, 11.41.

2-[1-(4-Chlorophenyl)ethenyl]-4-methoxy-1-(methylsulfonyl)benzene (3h): a colorless amorphous powder; R_f 0.29 (Et_2O/hexane 2:1); IR (neat) 1614, 1311, 1123 cm^{-1}; ^1H NMR δ 2.73 (s, 3H), 3.87 (s, 3H), 5.31 (s, 1H), 5.88 (s, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 44.6, 55.7, 113.1, 116.6, 118.0, 128.0, 128.5, 130.7, 132.2, 133.9, 138.2, 143.0, 145.8, 163.2. HR-MS (DART). Calcd for $C_{16}H_{16}ClO_3S$ (M+H): 323.0508. Found: *m*/*z* 323.0503.

1,2-Dimethoxy-4-(methylsulfonyl)-5-(1-phenylethenyl)benzene (3i): a colorless amorphous powder; R_f 0.30 (Et_2O/hexane 3:5); IR (KBr) 1622, 1341, 1131 cm^{-1}; ^1H NMR δ 2.72 (s, 3H), 3.93 (s, 3H), 3.98 (s, 3H), 5.37 (s, 1H), 5.96 (s, 1H), 6.81 (s, 1H), 7.27–7.33 (m, 5H), 7.61 (s, 1H); ^{13}C NMR δ 44.2, 56.3 (2 overlapped Cs), 111.8, 114.7, 116.8, 126.8, 128.1, 128.4, 130.7, 135.2, 139.9, 146.3, 148.2, 152.4.

HR-MS (DART). Calcd for $C_{17}H_{22}NO_4S$ (M+NH_4): 336.1264. Found: *m*/*z* 336.1248.

1-(1-Methylethenyl)-2-(methylsulfonyl)benzene (3j): a white solid; mp 108–110 ˚C (hexane/Et_2O); IR (KBr) 1637, 1297, 1129 cm^{-1}; ^1H NMR δ 2.13 (s, 3H), 3.07 (s, 3H), 4.86 (s, 1H), 5.27 (q, *J* = 1.1 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.39 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 26.0, 44.8, 116.1, 127.6, 129.1, 130.6, 133.4, 137.9, 144.2, 145.6. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34. Found: C, 61.20; H, 6.35; S, 16.36.

General Procedure for the Preparation of 3,4-Dihydro-2*H*-1-benzothiopyran 1,1-Dioxides (6). To a stirred solution of LDA (1.0 mmol), generated by the standard method from *n*-BuLi and *i*-Pr_2NH), in THF (4 mL) at –78 ˚C was added a solution of **3** (1.0 mmol) in THF (1 mL) dropwise. The temperature was gradually warmed to 0 ˚C or rt (see Table 1). The mixture was worked up as described for the preparation of **2a**. Purification of the crude product by column chromatography on SiO_2 gave **6**.

4-Phenyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6a): a white solid; mp 112–114 ˚C (hexane/CH_2Cl_2); IR (KBr) 1303, 1124 cm^{-1}; ^1H NMR δ 2.60–2.67 (m, 1H), 2.79–2.85 (m, 1H), 3.33 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 3.42 (ddd, *J* = 13.7, 9.1, 2.9 Hz, 1H), 4.34 (dd, *J* = 7.4, 5.2 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 7.09 (dd, *J* = 6.9, 1.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 7.4, 6.9 Hz, 2H), 7.41 (td, *J* = 7.4, 1.7 Hz, 1H), 7.45 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR δ 29.9, 44.3, 48.3, 123.5, 127.3, 128.1, 128.5, 128.9, 130.8, 132.4, 138.6, 139.3, 143.0. HR-MS (DART). Calcd for $C_{15}H_{15}O_2S$ (M+H): 259.0793. Found: *m*/*z* 259.0787. Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.50; H, 5.41; S, 12.31.

4-(3-Methylphenyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6b): a white solid; mp 108–110 ˚C (hexane/CH_2Cl_2); IR (KBr) 1307, 1120 cm^{-1}; ^1H NMR δ 2.32 (s, 3H), 2.60–2.67 (m, 1H), 2.77–2.83 (m, 1H), 3.33 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 3.44 (ddd, *J* = 13.7, 9.2, 2.9 Hz, 1H), 4.30 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.41 (td, *J* = 7.4, 1.7 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.99 (dd, *J* = 7.4, 1.7 Hz, 1H); ^{13}C NMR δ 21.4, 29.8, 44.3, 48.3, 123.4, 125.7, 128.0 (2 overlapped Cs), 128.8, 129.2, 130.9, 132.4, 138.71, 138.73, 139.2, 143.0. HR-MS (DART). Calcd for $C_{16}H_{17}O_2S$ (M+H): 273.0949. Found: *m*/*z* 273.0947. Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.45; H, 6.05; S, 11.65.

4-(4-Methylphenyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6c): a white solid; mp 163–164 ˚C (hexane/CH_2Cl_2); IR (KBr) 1306, 1149 cm^{-1}; ^1H NMR δ 2.34 (s, 3H), 2.58–2.65 (m, 1H), 2.76–2.83 (m, 1H), 3.32 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 3.43 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 4.31 (dd, *J* = 7.4, 5.2 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.40 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR δ 21.0, 29.9, 43.9, 48.2, 123.4, 128.0, 128.4, 129.6, 130.8, 132.3, 137.0, 138.8, 139.1, 140.0. HR-MS (DART). Calcd for $C_{16}H_{17}O_2S$ (M+H): 273.0949. Found: *m*/*z* 273.0945. Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S,

11.77. Found: C, 70.26; H, 6.05; S, 11.80.

4-(3-Chlorophenyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6d): a colorless amorphous powder; R_f 0.40 (Et_2O/hexane 2:1); IR (neat) 1308, 1150 cm^{-1}; ^1H NMR δ 2.60–2.67 (m, 1H), 2.77–2.84 (m, 1H), 3.35 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 3.41 (ddd, *J* = 13.7, 8.6, 2.9 Hz, 1H), 4.32 (dd, *J* = 7.4, 5.2 Hz, 1H), 6.95–6.99 (m, 2H), 7.13 (s, 1H), 7.26–7.29 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 29.8, 44.0, 48.2, 123.7, 126.7, 127.6, 128.4, 128.6, 130.3, 130.7, 132.6, 134.8, 137.8, 139.2, 145.0. HR-MS (DART). Calcd for $C_{15}H_{14}ClO_2S$ (M+H): 293.0403. Found: *m*/*z* 293.0398.

4-(4-Chlorophenyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6e): a colorless amorphous powder; R_f 0.37 (Et_2O/hexane 8:5); IR (KBr) 1306, 1152 cm^{-1}; ^1H NMR δ 2.58–2.64 (m, 1H), 2.78–2.81 (m, 1H), 3.32–3.42 (m, 2H), 4.31 (dd, *J* = 7.4, 5.2 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 29.9, 43.8, 48.3, 123.7, 128.3, 129.2, 129.9, 130.7, 132.5, 133.3, 138.1, 139.3, 141.5. HR-MS (DART). Calcd for $C_{15}H_{14}ClO_2S$ (M+H): 293.0403. Found: *m*/*z* 293.0391.

4-(4-Methoxyphenyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6f): a pale-yellow gum; R_f 0.34 (Et_2O/hexane 8:5); IR (neat) 1610, 1309, 1125 cm^{-1}; ^1H NMR δ 2.59–2.65 (m, 1H), 2.76–2.82 (m, 1H), 3.33 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 3.43 (ddd, *J* = 13.7, 9.1, 2.9 Hz, 1H), 3.80 (s, 3H), 4.30 (dd, *J* = 7.4, 5.2 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 29.9, 43.5, 48.3, 55.3, 114.3, 123.4, 128.0, 129.5, 130.8, 132.3, 135.0, 139.0, 139.1, 158.7. HR-MS (DART). Calcd for $C_{16}H_{17}O_3S$ (M+H): 289.0898. Found: *m*/*z* 289.0885.

6-Methoxy-4-phenyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6g): a colorless amorphous powder; R_f 0.35 (Et_2O/hexane 5:2); IR (KBr) 1599, 1333, 1128 cm^{-1}; ^1H NMR δ 2.59–2.65 (m, 1H), 2.79–2.83 (m, 1H), 3.29 (ddd, *J* = 13.7, 9.2, 2.9 Hz, 1H), 3.39 (ddd, *J* = 13.7, 9.7, 2.9 Hz, 1H), 3.72 (s, 3H), 4.30 (dd, *J* = 9.7, 9.2 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 6.97 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.93 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR δ 30.0, 44.5, 48.2, 55.4, 114.1, 115.2, 125.6, 127.3, 128.5, 128.9, 131.4, 140.8, 142.8, 162.2. HR-MS (DART). Calcd for $C_{16}H_{17}O_3S$ (M+H): 289.0898. Found: *m*/*z* 289.0893. Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.52; H, 5.82; S, 11.13.

4-(4-Chlorophenyl)-6-methoxy-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6h): a white solid; mp 124–126 °C (hexane/CH_2Cl_2); IR (KBr) 1606, 1330, 1117 cm^{-1}; ^1H NMR δ 2.55–2.62 (m, 1H), 2.75–2.81 (m, 1H), 3.31 (ddd, *J* = 13.7, 9.2, 2.9 Hz, 1H), 3.36 (ddd, *J* = 13.7, 9.2, 2.9 Hz, 1H), 3.73 (s, 3H), 4.27 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.39 (d, *J* = 2.3 Hz, 1H), 6.97 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H),

7.32 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 29.9, 43.9, 48.2, 55.5, 114.1, 115.2, 125.7, 129.1, 129.8, 131.4, 133.2, 140.4, 141.4, 162.3. HR-MS (DART). Calcd for $C_{16}H_{16}ClO_3S$ (M+H): 323.0508. Found: *m*/*z* 323.0503. Anal. Calcd for $C_{16}H_{15}ClO_3S$: C, 59.53; H, 4.68. Found: C, 59.33; H, 4.59.

6,7-Dimethoxy-4-phenyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6i): a white solid; mp 132–134 ˚C (hexane/CH_2Cl_2); IR (KBr) 1300, 1130 cm^{-1}; ^{1}H NMR δ 2.54–2.61 (m, 1H), 2.82–2.88 (m, 1H), 3.26 (ddd, *J* = 13.3, 9.0, 2.3 Hz, 1H), 3.36 (ddd, *J* = 13.3, 10.0, 2.3 Hz, 1H), 3.70 (s, 3H), 3.96 (s, 3H), 4.28 (dd, *J* = 6.3, 5.7 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.38 (s, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.38 (s, 1H); ^{13}C NMR δ 30.1, 44.0, 47.8, 56.0, 56.2, 104.3, 112.1, 127.3, 128.4, 128.9, 131.1, 131.8, 143.0, 149.0, 152.2. HR-MS (ESI). Calcd for $C_{17}H_{19}O_4S$ (M+H): 319.1004. Found: *m*/*z* 319.0999. Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 63.86; H, 5.73.

4-Methyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (6j): a white solid; mp 68–69 ˚C (hexane/CH_2Cl_2); IR (KBr) 1282, 1128 cm^{-1}; ^{1}H NMR δ 1.35 (d, *J* = 7.4 Hz, 3H), 2.17–2.23 (m, 1H), 2.53–2.60 (m, 1H), 3.09–3.13 (m, 1H), 3.25 (ddd, *J* = 13.7, 8.6, 2.9 Hz, 1H), 3.98 (ddd, *J* = 13.7, 10.3, 3.4 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.44 (td, *J* = 7.4, 1.1 Hz, 1H), 7.84 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 21.7, 28.3, 31.7, 47.8, 123.6, 127.5, 128.7, 132.5, 137.9, 141.1. HR-MS (DART). Calcd for $C_{10}H_{13}O_2S$ (M+H): 197.0636. Found: *m*/*z* 197.0632. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34. Found: C, 61.07; H, 6.16; S, 16.20.

General Procedure for the Preparation of 4-Alkyl-4-aryl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxides 7. After compound **3** (1.0 mmol) was treated with LDA (1.0 mmol) in THF (9 mL) as described for the preparation of **6**, one of the electrophiles (1.0 mmol) was added dropwise. The characteristic dark red color gradually faded within 10 min. The mixture was worked up as described for the preparation of **2a** and the crude product was purified by column chromatography on SiO_2 or recrystallization to afford **7**.

4-Methyl-4-phenyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7a-i): a colorless amorphous powder; R_f 0.28 (AcOEt/hexane 3:10); IR (KBr) 1290, 1120 cm^{-1}; ^{1}H NMR δ 1.85 (s, 3H), 2.63 (ddd, *J* = 15.5, 10.3, 2.9 Hz, 1H), 2.73 (ddd, *J* = 15.5, 9.2, 2.9 Hz, 1H), 3.24 (ddd, *J* = 14.3, 10.3, 2.9 Hz, 1H), 3.35 (ddd, *J* = 14.3, 9.2, 2.9 Hz, 1H), 7.08–7.11 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.45–7.47 (m, 2H), 7.99–8.00 (m, 1H); ^{13}C NMR δ 29.1, 37.7, 42.9, 47.1, 123.5, 126.9, 127.0, 127.8, 128.6, 130.0, 132.5, 138.6, 143.6, 147.2. HR-MS (DART). Calcd for $C_{16}H_{17}O_2S$ (M+H): 273.0949. Found: *m*/*z* 273.0937.

4-Phenyl-4-(phenylmethyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7a-ii): a pale-yellow solid; mp 192–194 ˚C (hexane/CH_2Cl_2); IR (KBr) 1288, 1123 cm^{-1}; ^{1}H NMR δ 2.70–2.77 (m, 2H), 2.88 (ddd, *J* = 16.0, 10.3, 4.0 Hz, 1H), 2.96 (ddd, *J* = 16.0, 11.2, 6.3 Hz, 1H), 3.55 (d, *J* = 13.7 Hz, 1H), 3.69 (d, *J* =

13.7 Hz, 1H), 6.82 (d, *J* = 7.4 Hz, 2H), 7.13–7.19 (m, 5H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.57 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR δ 34.6, 46.6, 47.3, 47.8, 123.8, 127.0, 127.2, 127.5, 128.0, 128.4, 128.6, 130.3, 131.2, 132.0, 136.4, 140.0, 141.2, 146.8. HR-MS (DART). Calcd for $C_{22}H_{21}O_2S$ (M+H): 349.1262. Found: *m*/*z* 349.1252. Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79; S, 9.20. Found: C, 73.89; H, 5.81; S, 9.14.

4-(Methylsulfanyl)-4-phenyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7a-iii): a pale-yellow solid; mp 164–166 ˚C (hexane/CH_2Cl_2); IR (KBr) 1289, 1126 cm^{-1}; ^{1}H NMR δ 1.96 (s, 3H), 2.97 (ddd, *J* = 14.9, 8.0, 1.7 Hz, 1H), 3.13 (ddd, *J* = 14.9, 9.9, 1.7 Hz, 1H), 3.20 (ddd, *J* = 15.5, 9.9, 1.7 Hz, 1H), 3.48 (ddd, *J* = 15.5, 8.0, 1.7 Hz, 1H), 7.26–7.34 (m, 5H), 7.50 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.53 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.57 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR δ 13.8, 35.9, 47.4, 55.5, 123.8, 127.8, 127.9, 128.76, 128.78, 131.9, 132.5, 138.5, 140.0, 143.0. HR-MS (DART). Calcd for $C_{16}H_{20}NO_2S_2$ (M+NH_4): 322.0930. Found: *m*/*z* 322.0923. Anal. Calcd for $C_{16}H_{16}O_2S_2$: C, 63.13; H, 5.30. Found: C, 63.03; H, 5.29.

4-(3-Methylphenyl)-4-(prop-2-enyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7b): a white solid; mp 135–137 ˚C (hexane/CH_2Cl_2); IR (KBr) 1634, 1290, 1130 cm^{-1}; ^{1}H NMR δ 2.30 (s, 3H), 2.48 (ddd, *J* = 14.9, 6.9, 2.3 Hz, 1H), 2.97–3.03 (m, 2H), 3.09 (dd, *J* = 14.9, 5.7 Hz, 1H), 3.16–3.27 (m, 2H), 5.10 (d, *J* = 9.7 Hz, 1H), 5.19 (d, *J* = 16.6 Hz, 1H), 5.51–5.60 (m, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.21 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.48–7.54 (m, 2H), 8.03 (dd, *J* = 7.4, 2.3 Hz, 1H); ^{13}C NMR δ 21.6, 34.2, 45.7, 46.1, 46.7, 119.2, 123.8, 124.5, 127.7, 127.8, 128.0, 128.5, 130.2, 132.3, 133.4, 138.4, 139.8, 140.7, 146.3. HR-MS (DART). Calcd for $C_{19}H_{21}O_2S$ (M+H): 313.1262. Found: *m*/*z* 313.1257. Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.26. Found: C, 72.97; H, 6.54; S, 10.19.

4-(3-Chlorophenyl)-4-(phenylmethyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7d): a colorless amorphous powder; R_f 0.25 (Et_2O/hexane 1:2); IR (KBr) 1292, 1128 cm^{-1}; ^{1}H NMR δ 2.69–2.76 (m, 2H), 2.83–2.98 (m, 2H), 3.50 (d, *J* = 13.7 Hz, 1H), 3.66 (d, *J* = 13.7 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 2H), 6.97–7.01 (m, 1H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.23–7.27 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.60 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 34.5, 46.5, 47.1, 47.9, 123.9, 126.3, 127.3, 127.35, 127.49, 128.35, 128.44, 129.9, 130.2, 131.1, 132.2, 134.6, 135.9, 139.9, 140.6, 149.1. HR-MS (DART). Calcd for $C_{22}H_{20}ClO_2S$ (M+H): 383.0872. Found: *m*/*z* 383.0866.

6-Methoxy-4-phenyl-4-(prop-2-enyl)-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7g): a white solid; mp 157–160 ˚C (hexane/CH_2Cl_2); IR (KBr) 1635, 1294, 1147 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43–2.47 (m, 1H), 2.97–3.22 (m, 5H), 3.79 (s, 3H), 5.13 (d, *J* = 10.3 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H),

5.59–5.63 (m, 1H), 6.67 (s, 1H), 7.02 (d, J = 9.2 Hz, 1H), 7.05 (d, J = 7.4 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.98 (d, J = 9.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.5, 45.6, 46.4, 46.7, 55.5, 113.7, 115.1, 119.6, 125.9, 127.0, 127.1, 128.7, 132.2, 133.4, 142.8, 146.1, 162.2. HR-MS (DART). Calcd for $C_{19}H_{21}O_3S$ (M+H): 329.1211. Found: *m/z* 329.1206. Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14; S, 9.76. Found: C, 69.50; H, 6.21; S, 9.81.

4-(4-Chlorophenyl)-6-methoxy-4-methyl-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide (7h): a white solid; mp 161–163 ˚C (hexane/CH_2Cl_2); IR (KBr) 1293, 1120 cm^{-1}; ^{1}H NMR δ 1.82 (s, 3H), 2.59 (ddd, J = 14.9, 9.2, 2.3 Hz, 1H), 2.69 (dd, J = 14.9, 9.7, 2.9 Hz, 1H), 3.19 (ddd, J = 13.7, 9.7, 2.3 Hz, 1H), 3.33 (ddd, J = 13.7, 9.2, 2.9 Hz, 1H), 3.76 (s, 3H), 6.48 (d, J = 2,3 Hz, 1H), 6.98 (dd, J = 8.6, 2.3 Hz, 1H), 7.06 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ 29.0, 37.8, 42.8, 47.0, 55.5, 113.5, 115.0, 125.8, 128.5, 128.7, 140.8, 132.8, 145.4, 145.7, 162.4. HR-MS (DART). Calcd for $C_{17}H_{18}ClO_3S$ (M+H): 337.0665. Found: *m/z* 337.0659. Anal. Calcd for $C_{17}H_{17}ClO_3S$: C, 60.62; H, 5.09. Found: C, 60.48; H, 5.11.

ACKNOWLEDGEMENTS

The authors are indebted to Mrs. Miyuki Tanmatsu of this university for recording mass spectra and performing combustion analyses.

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