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SYNTHESIS OF 2*H*-BENZO[*b*]THIETES BY TFA-MEDIATED CYCLIZATION OF *O*-*tert*-BUTYL *S*-(2-VINYLPHENYL) CARBONOTHIOATES VIA 4*H*-3,1-BENZOXATHIIN-2-ONE INTERMEDIATES

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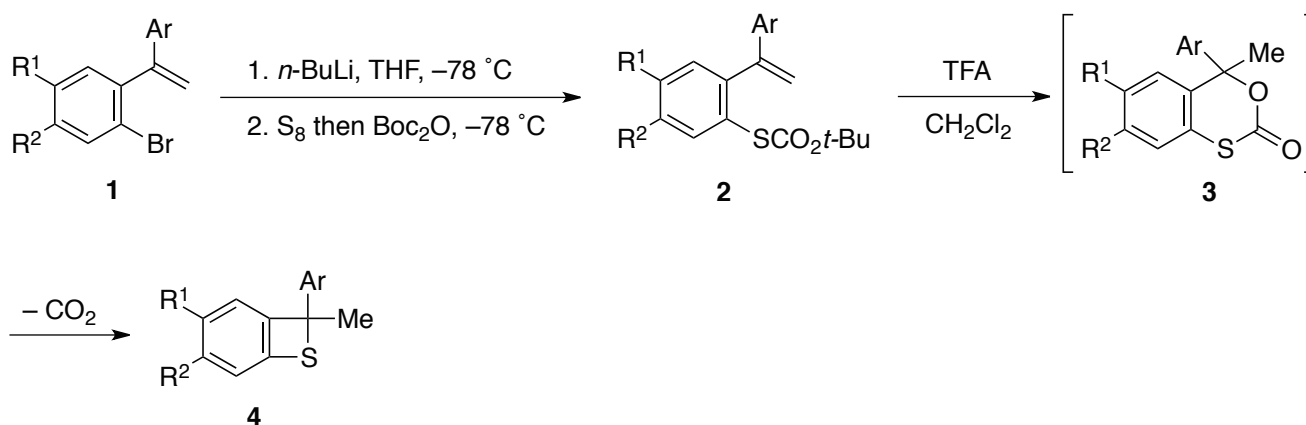
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Abstract – An efficient method for the preparation of 2*H*-benzo[*b*]thiete derivatives under mild conditions has been developed. The reaction of 2-(1-arylethenyl)phenyl bromides with butyllithium at $-78\text{ }^{\circ}\text{C}$ generates 2-(1-arylethenyl)phenyllithiums, which are successively treated with sulfur and Boc_2O at the same temperature to afford *S*-[2-(1-arylethenyl)phenyl] *O*-*tert*-butyl carbonothioates. These compounds are then treated with TFA at 0 or $20\text{ }^{\circ}\text{C}$ to yield 2-aryl-2-methyl-2*H*-benzo[*b*]thietes *via* formation of the 4-aryl-4-methyl-4*H*-3,1-benzoxathiin-2-ones followed by decarboxylation.

2*H*-Benzo[*b*]thiete (7-thiabicyclo[4.2.0]octa-1,3,5-triene) derivatives¹ are known to be convenient synthetic precursors for useful sulfur containing heterocycles,² such as 4*H*-3,1,2-benzoxathiazines^{2a} and 3,4-dihydro-2*H*-1-benzopyrans.^{2b,e} A usual method for the preparation of 2*H*-benzo[*b*]thiete derivatives is the thermal decarboxylation of 4*H*-3,1-benzoxathiin-2-one derivatives,³ which are synthesized by the reactions of *o*-sulfanylbenzyl alcohols with carbonylation agents, such as diphosgene^{3a} or *N,N'*-carbonyldiimidazole.⁴ About two decades ago, Okuma and co-workers reported that 2-mono- and 2,2-disubstituted 2*H*-benzo[*b*]thietes could be efficiently prepared by the reaction of benzynes with thioaldehydes or thiones.⁵ Meanwhile, we have been interested in developing facile methods for the synthesis of heterocyclic compounds utilizing the reactions of 2-(1-arylethenyl)phenyllithiums, which can easily be generated by the bromine/lithium exchange between 2-(1-arylethenyl)phenyl bromides and butyllithium, with a variety of electrophiles.⁶ Recently, we have reported on the synthesis of

2*H*-3,4-dihydro-1-benzothiopyran 1,1-dioxides based on the reaction of these lithium compounds with sulfur.⁷ In the course of these studies, we wish to report a new and facile method for the preparation of 2-aryl-2-methyl-2*H*-benzo[*b*]thietes (**4**) from 2-(1-arylethenyl)phenyl bromides (**1**). The method is based on the treatment of *S*-[2-(1-arylethenyl)phenyl] *O*-*tert*-butyl carbonothioates (**2**), which can be easily obtained by successive treatment of **1** with butyllithium, sulfur, and di-*tert*-butyl dicarbonate (Boc₂O), with trifluoroacetic acid (TFA) under mild conditions. Generation of the intermediates, 4*H*-3,1-benzoxathiin-2-one derivatives (**3**), is also discussed.

The preparation of **4** from **1** *via* **2** was conducted according to the sequence illustrated in Scheme 1. In order to obtain carbonothioates (**2**), 2-(1-arylethenyl)phenyllithiums, generated by the bromine/lithium exchange between **1** and butyllithium in THF at -78 °C, were allowed to react successively with sulfur and Boc₂O at the same temperature. After aqueous work up and the subsequent purification of the crude products by column chromatography on silica gel, the desired carbonothioates (**2**) could be obtained. The results are listed in Table 1. As can be seen from it, the yields of the products are moderate in general.



Scheme 1

Table 1. Preparation of 2*H*-benzo[*b*]thietes (**4**)

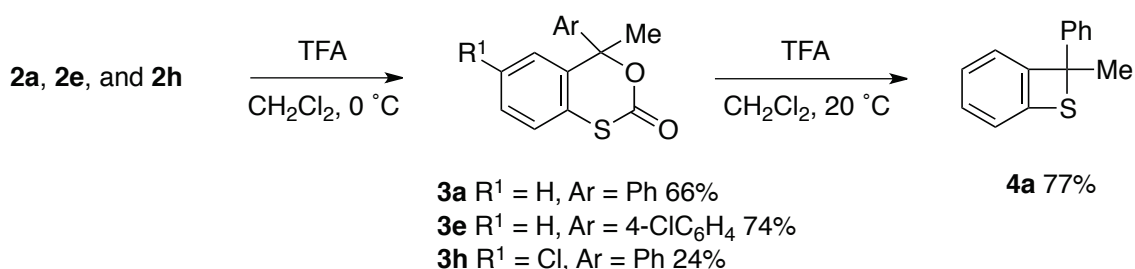
| Entry | 1 | R ¹ | R ² | Ar | 2 | Yield/% ^a | Temp/°C | 4 | Yield/% ^a |
|-------|-----------|----------------|----------------|------------------------------------|-----------|----------------------|---------|-----------|----------------------|
| 1 | 1a | H | H | Ph | 2a | 54 | 20 | 4a | 53 |
| 2 | 1b | H | H | 3-MeC ₆ H ₄ | 2b | 63 | 20 | 4b | 57 |
| 3 | 1c | H | H | 4-MeC ₆ H ₄ | 2c | 48 | 20 | 4c | 43 |
| 4 | 1d | H | H | 3-ClC ₆ H ₄ | 2d | 50 | 20 | 4d | 45 |
| 5 | 1e | H | H | 4-ClC ₆ H ₄ | 2e | 50 | 20 | 4e | 67 |
| 6 | 1f | H | H | 4-MeOC ₆ H ₄ | 2f | 54 | 0 | 4f | 43 |
| 7 | 1g | H | Cl | Ph | 2g | 41 | 0 | 4g | 40 |
| 8 | 1h | Cl | H | Ph | 2h | 54 | 20 | 4h | 36 |
| 9 | 1i | MeO | H | 4-ClC ₆ H ₄ | 2i | 50 | 0 | 4i | 82 |
| 10 | 1j | MeO | H | 4-MeOC ₆ H ₄ | 2j | 42 | 0 | 4j | 90 |
| 11 | 1k | MeO | MeO | Ph | 2k | 60 | 0 | 4k | 80 |

^a Yields of isolated products.

The transformation of carbonothioates (**2**) into 2*H*-benzo[*b*]thietes (**4**) was carried out by adding excess trifluoroacetic acid (TFA) to solutions of **2** in dichloromethane at the temperatures indicated in Table 1. It appeared to proceed *via* the formation of 4*H*-3,1-benzoxathiin-2-one intermediates (**3**), as judged from monitoring of the progress of the reactions by TLC analyses on silica gel (*vide infra*). After completion of the reactions, the resulting mixtures were diluted with dichloromethane and excess amounts of anhydrous potassium carbonate were added to remove excess TFA. The precipitates were removed by filtration under reduced pressure and the filtrates were concentrated by evaporation. The crude residues were purified by column chromatography on silica gel or trituration to give the desired products (**4**) (For details, see Experimental).

The results are shown in Table 1 as well. The products were obtained in generally moderate yields (Entries 1-8). In the cases of conducting reactions at 20 °C using substrates (**2a-e**) and (**2h**) (Entries 1-5 and 8), the higher temperatures than 20 °C did result in decreased yields. The reactions using substrates (**2f**), (**2g**), and (**2i-k**) could be conducted at 0 °C (Entries 6, 7, and 9-11). Especially, those using substrates (**2i**) and (**2j**) proceeded rapidly and cleanly at this temperature, and we could not be observed the corresponding intermediate 4*H*-3,1-benzoxathiin-2-ones (**3i**) and (**3j**) by TLC analyses. The desired products (**4i**) and (**4j**), respectively, were easily isolated in spectroscopically pure forms by trituration of the crude products with hexane in good yields (Entries 9 and 10). When substrate (**2k**) was used, the rate of the formation of the desired products (**4k**) somewhat reduced compared to those using **2i** and **2j** and the corresponding 4*H*-3,1-benzoxathiin-2-one intermediate (**3k**) was observed at an early stage of the reaction by TLC analyses on silica gel. The product could also be isolated by trituration and its yield was good (Entry 11). Presumably, an electron-donating methoxy substituent *para* to the carbonothioate function facilitates the present acid-assisted decarboxylation from the benzoxathiinone intermediates due to the resonance effect.

In order to clarify the intermediacy of 4*H*-3,1-benzoxathiin-2-ones (**3**), the reactions using **2a**, **2e**, and **2h** were conducted at 0 °C and the corresponding benzoxathiinones (**3a**), (**3e**), and (**3h**), respectively, could be isolated. As a matter of fact, the transformation of **3a** into **4a** on treatment with TFA under the above conditions could be achieved in 77% yield. These results are illustrated in Scheme 2.



Scheme 2

In conclusion, we have demonstrated that a facile preparation of 2-aryl-2-methyl-2*H*-benzo[*b*]thietes can be achieved by treating *S*-[2-(1-arylethenyl)phenyl] *O*-*tert*-butyl carbonothioates, easily derived from 2-(1-arylethenyl)phenyl bromides, with TFA through formation of the corresponding 4*H*-3,1-benzoxathiin-2-one intermediates followed by acid-assisted decarboxylation. The present method may be of value in organic synthesis, because 1) the manipulations are very simple, 2) the starting materials are readily available, and 3) the reaction can be conducted using inexpensive reagents under mild conditions.

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 or ESI, both positive) or a JEOL JMS-T100GCV (FI, TOF; 2100V) spectrometer. 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. 1-(1-Arylethenyl)-2-bromobenzenes (**1a**),⁸ (**1b**),^{6c} (**1c**),^{6d} (**1d**),⁹ (**1e**),^{6a} (**1f**),^{6b} (**1g**),¹⁰ (**1h**),^{6h} (**1i**),^{6c} (**1j**),^{6c} and (**1k**)^{6c} 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 Carbonothioates (2). *O*-(1,1-Dimethylethyl) *S*-[2-(1-Phenylethenyl)phenyl] Carbonothioate (**2a**). To a stirred solution of **1a** (0.57 g, 2.2 mmol) in THF (7 mL) at -78 °C was added *n*-BuLi (1.6 M in hexane, 2.2 mmol) dropwise. After 10 min, a THF (7 mL) solution of S₈ (71 mg, 0.28 mmol) and (Boc)₂O (0.48 g, 2.2 mmol) were successively added, and stirring was continued for an additional 5 min. Saturated aqueous NH₄Cl (30 mL) was added and the mixture was extracted with AcOEt (3 × 25 mL). The combined extracts were washed with saturated aqueous NaHCO₃ (2 × 20 mL) and brine (20 mL), dried (Na₂SO₄), and concentrated by evaporation. The residue was purified by column chromatography on SiO₂ to give **2a** (0.37 g, 54%); a colorless oil; *R*_f 0.25 (CH₂Cl₂/hexane 1:10); IR (neat) 1724, 1615 cm⁻¹; ¹H NMR δ 1.38 (s, 9H), 5.22 (s, 1H), 5.81 (s, 1H), 7.23–7.28 (m, 5H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.40 (d, *J* = 7.4, 6.9 Hz, 1H), 7.44 (dd, *J* = 7.4, 6.9 Hz, 1H), 7.62 (d, *J* = 6.9 Hz, 1H); ¹³C NMR δ 28.0, 85.0, 116.0, 126.6, 127.5, 127.8, 128.19, 128.24, 129.7, 130.8, 137.1, 140.2, 146.4, 148.2, 167.6. HR-MS (ESI). Calcd for C₁₉H₂₀NaO₂S: (M+Na): 335.1082. Found: *m/z*

335.1072.

***O*-(1,1-Dimethylethyl) *S*-{2-[1-(3-Methylphenyl)ethenyl]phenyl} Carbonothioate (2b):** a colorless oil; R_f 0.19 (CH₂Cl₂/hexane 1:10); IR (neat) 1727 cm⁻¹; ¹H NMR δ 1.38 (s, 9H), 2.28 (s, 3H), 5.18 (d, J = 1.1 Hz, 1H), 5.79 (d, J = 1.1 Hz, 1H), 7.02–7.05 (m, 3H), 7.15 (t, J = 7.4 Hz, 1H), 7.33 (dd, J = 7.4, 1.7 Hz, 1H), 7.39 (td, J = 7.4, 1.7 Hz, 1H), 7.42 (td, J = 7.4, 1.7 Hz, 1H), 7.62 (dd, J = 7.4, 1.7 Hz, 1H); ¹³C NMR δ 21.4, 28.0, 85.0, 115.8, 123.8, 127.2, 127.8, 128.1, 128.2, 128.4, 129.6, 130.8, 137.0, 137.7, 140.2, 146.5, 148.3, 167.6. HR-MS (DART). Calcd for C₂₀H₂₃O₂S: (M+H): 327.1419. Found: m/z 327.1433.

***O*-(1,1-Dimethylethyl) *S*-{2-[1-(4-Methylphenyl)ethenyl]phenyl} Carbonothioate (2c):** a colorless oil; R_f 0.24 (CH₂Cl₂/hexane 1:10); IR (neat) 1727, 1609 cm⁻¹; ¹H NMR δ 1.38 (s, 9H), 2.31 (s, 3H), 5.15 (s, 1H), 5.76 (s, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.4 Hz, 1H), 7.38 (td, J = 7.4, 1.7 Hz, 1H), 7.42 (dd, J = 7.4, 1.7 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H); ¹³C NMR δ 21.1, 28.0, 85.0, 115.0, 126.5, 127.8, 128.1, 128.9, 129.6, 130.8, 137.0, 137.3, 137.5, 146.6, 148.1, 167.7. HR-MS (DART). Calcd for C₂₀H₂₃O₂S: (M+H): 327.1419. Found: m/z 327.1413.

***S*-{2-[1-(3-Chlorophenyl)ethenyl]phenyl} *O*-(1,1-Dimethylethyl) Carbonothioate (2d):** a colorless oil; R_f 0.27 (CH₂Cl₂/hexane 1:11); IR (neat) 1727 cm⁻¹; ¹H NMR δ 1.38 (s, 9H), 5.26 (s, 1H), 5.80 (s, 1H), 7.09 (dd, J = 7.4, 1.7 Hz, 1H), 7.16–7.24 (m, 3H), 7.34 (dd, J = 7.4, 1.7 Hz, 1H), 7.41 (td, J = 7.4, 1.7 Hz, 1H), 7.43 (td, J = 7.4, 1.7 Hz, 1H), 7.61 (d, J = 7.4, 1H); ¹³C NMR δ 28.0, 85.2, 117.2, 124.9, 126.6, 127.6, 127.8, 128.6, 129.4, 129.8, 130.8, 134.2, 137.3, 142.2, 145.7, 147.3, 167.3. HR-MS (DART). Calcd for C₁₉H₂₃ClNO₂S: (M+NH₄): 364.1138. Found: m/z 364.1133.

***S*-{2-[1-(4-Chlorophenyl)ethenyl]phenyl} *O*-(1,1-Dimethylethyl) Carbonothioate (2e):** a colorless oil; R_f 0.17 (CH₂Cl₂/hexane 1:11); IR (neat) 1723, 1616 cm⁻¹; ¹H NMR δ 1.38 (s, 9H), 5.23 (s, 1H), 5.77 (s, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 7.35 (dd, J = 7.4, 1.7 Hz, 1H), 7.41 (td, J = 7.4, 1.4 Hz, 1H), 7.45 (td, J = 7.4, 1.7 Hz, 1H), 7.61 (dd, J = 7.4, 1.7 Hz, 1H); ¹³C NMR δ 28.0, 85.2, 116.5, 127.7, 127.9, 128.3, 128.5, 129.9, 130.8, 133.3, 137.3, 138.8, 145.9, 147.3, 167.4. HR-MS (DART). Calcd for C₁₉H₂₃ClNO₂S: (M+NH₄): 364.1138. Found: m/z 364.1124.

***O*-(1,1-Dimethylethyl) *S*-{2-[1-(4-Methoxyphenyl)ethenyl]phenyl} Carbonothioate (2f):** a colorless oil; R_f 0.30 (Et₂O/hexane 1:15); IR (neat) 1723, 1607 cm⁻¹; ¹H NMR δ 1.38 (s, 9H), 3.77 (s, 3H), 5.10 (s, 1H), 5.71 (s, 1H), 6.79 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 6.9 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.43 (dd, J = 7.4, 6.9 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H); ¹³C NMR δ 28.0, 55.2, 85.0, 113.5, 114.0, 127.8, 128.1, 129.6, 130.7, 133.0, 137.0, 146.6, 146.7, 147.6, 159.1, 167.7. HR-MS (DART). Calcd for C₂₀H₂₃O₃S: (M+H): 343.1368. Found: m/z 343.1363.

***S*-[5-Chloro-2-(1-phenylethenyl)phenyl] *O*-(1,1-Dimethylethyl) Carbonothioate (2g):** a colorless oil; R_f 0.26 (CH₂Cl₂/hexane 1:20); IR (neat) 1728 cm⁻¹; ¹H NMR δ 1.39 (s, 9H), 5.20 (s, 1H), 5.81 (s, 1H),

7.21 (d, $J = 8.0$ Hz, 2H), 7.24–7.28 (m, 4H), 7.39 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.63 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR δ 28.0, 85.6, 116.5, 126.5, 127.8, 128.3, 129.68, 129.73, 131.8, 133.5, 136.4, 139.9, 144.6, 147.3, 166.7. HR-MS (DART). Calcd for $\text{C}_{19}\text{H}_{23}\text{ClNO}_2\text{S}$: ($\text{M}+\text{NH}_4$): 364.1138. Found: m/z 364.1133.

S-[4-Chloro-2-(1-phenylethenyl)phenyl] O-(1,1-Dimethylethyl) Carbonothioate (2h): a colorless oil; R_f 0.27 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:15); IR (neat) 1725 cm^{-1} ; ^1H NMR δ 1.38 (s, 9H), 5.22 (s, 1H), 5.81 (s, 1H), 7.21–7.29 (m, 5H), 7.35 (d, $J = 2,3$ Hz, 1H), 7.37 (dd, $J = 8.0, 2.3$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR δ 28.0, 85.4, 116.6, 126.3, 126.6, 127.8, 128.3, 128.4, 130.7, 135.8, 138.2, 139.6, 147.3, 147.9, 167.1. HR-MS (DART). Calcd for $\text{C}_{19}\text{H}_{23}\text{ClNO}_2\text{S}$: ($\text{M}+\text{NH}_4$): 364.1138. Found: m/z 364.1132.

S-{2-[1-(4-Chlorophenyl)ethenyl]-4-methoxyphenyl} O-(1,1-Dimethylethyl) Carbonothioate (2i): a white solid; mp 80–82 °C (hexane); IR (KBr) $1723, 1622\text{ cm}^{-1}$; ^1H NMR δ 1.36 (s, 9H), 3.83 (s, 3H), 5.23 (s, 1H), 5.75 (s, 1H), 6.88 (d, $J = 2.9$ Hz, 1H), 6.94 (dd, $J = 8.6, 2.9$ Hz, 1H), 7.17 (d, $J = 8.6$ Hz, 2H), 7.22 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 1H); ^{13}C NMR δ 28.0, 55.4, 85.0, 114.1, 116.2, 116.4, 118.6, 128.0, 128.3, 133.4, 138.7, 138.9, 147.5, 147.7, 160.8, 168.1. Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{ClO}_3\text{S}$: C, 63.74; H, 5.62; S, 8.51. Found: C, 63.38; H, 5.76; S, 8.89.

O-(1,1-Dimethylethyl) S-{4-Methoxy-2-[1-(4-methoxyphenyl)ethenyl]phenyl} Carbonothioate (2j): a colorless oil; R_f 0.47 ($\text{Et}_2\text{O}/\text{hexane}$ 1:5); IR (neat) $1723, 1607\text{ cm}^{-1}$; ^1H NMR δ 1.37 (s, 9H), 3.77 (s, 3H), 3.82 (s, 3H), 5.10 (s, 1H), 5.68 (s, 1H), 6.79 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 2.9$ Hz, 1H), 6.93 (dd, $J = 8.6, 2.9$ Hz, 1H), 7.18 (d, $J = 8.6$ Hz, 2H), 7.50 (d, $J = 8.6$ Hz, 1H); ^{13}C NMR δ 28.0, 55.2, 55.4, 84.7, 113.5, 113.8, 113.9, 116.2, 118.7, 127.8, 132.8, 138.6, 147.7, 148.4, 159.2, 160.7, 168.4. HR-MS (DART). Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_4\text{S}$ ($\text{M}+\text{H}$): 373.1473. Found: m/z 373.1469.

S-[4,5-Dimethoxy-2-(1-phenylethenyl)phenyl] O-(1,1-Dimethylethyl) Carbonothioate (2k): a colorless oil; R_f 0.24 ($\text{Et}_2\text{O}/\text{hexane}$ 1:4); IR (neat) $1723, 1615\text{ cm}^{-1}$; ^1H NMR δ 1.38 (s, 9H), 3.87 (s, 3H), 3.92 (s, 3H), 5.21 (s, 1H), 5.79 (s, 1H), 6.82 (s, 1H), 7.07 (s, 1H), 7.23–7.26 (m, 5H); ^{13}C NMR δ 28.0, 56.0, 56.1, 84.9, 113.3, 115.8, 118.5, 119.3, 126.6, 127.5, 128.2, 140.0, 140.4, 148.1, 148.4, 150.2, 168.1. HR-MS (DART). Calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_4\text{S}$: ($\text{M}+\text{NH}_4$): 390.1734. Found: m/z 390.1724.

General Procedure for the Preparation of 2H-Benzo[*b*]thietes (7-Thiabicyclo[4.2.0]octa-1,3,5-trienes) (4). To a stirred solution of one of the compounds (2) (1.0 mmol) in CH_2Cl_2 (70 μL) at 0 °C was added TFA (0.5 mL). Stirring was continued at the temperature indicated in Table 1 until disappearance of the spots due to the starting material [and the benzoxathiinone intermediate (3)] had been confirmed by TLC analyses (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{hexane}$ 3:5). The mixture was diluted with CH_2Cl_2 (20 mL) and anhydrous K_2CO_3 (2.0 g) was added. After 20 min vigorous stirring at the same temperature, the resulting mixture was filtrated through a Celite 545 pad, and the filtrate was concentrated by evaporation. The residue was purified by column chromatography on SiO_2 or trituration with hexane to afford 4.

8-Methyl-8-phenyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4a). This product was purified by column chromatography. It was slightly more mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A white solid; R_f 0.25 ($\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:5); mp 171–173 °C (hexane); IR (KBr) 1493 cm^{-1} ; ^1H NMR δ 2.08 (s, 3H), 6.96 (d, $J = 8.0$ Hz, 2H), 7.01 (t, $J = 7.4$ Hz, 1H), 7.12–7.18 (m, 4H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR δ 36.7, 60.7, 125.7, 126.9, 127.47, 127.52, 128.0, 129.1, 134.4, 140.1, 148.6, 148.9. HR-MS (DART). Calcd for $\text{C}_{14}\text{H}_{13}\text{S}$: (M+H): 213.0738. Found: m/z 213.0733. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{S}$: C, 79.20; H, 5.70. Found: C, 79.01; H, 5.91.

8-Methyl-8-(3-methylphenyl)-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4b). This product was purified by column chromatography. It was slightly more mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A colorless gum; R_f 0.28 ($\text{Et}_2\text{O}/\text{hexane}$ 1:70); IR (neat) 1487 cm^{-1} ; ^1H NMR δ 2.07 (s, 3H), 2.28 (s, 3H), 6.72 (d, $J = 7.4$ Hz, 1H), 6.88 (s, 1H), 6.98–7.15 (m, 4H), 7.27 (d, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR δ 21.5, 36.8, 60.7, 124.2, 126.4, 127.3, 127.4, 127.7, 127.9, 129.0, 134.5, 137.0, 140.2, 148.6, 149.1. HR-MS (DART). Calcd for $\text{C}_{15}\text{H}_{15}\text{S}$: (M+H): 227.0894. Found: m/z 227.0884.

8-Methyl-8-(4-methylphenyl)-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4c). This product was purified by column chromatography. It was slightly more mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A white solid; R_f 0.22 ($\text{Et}_2\text{O}/\text{hexane}$ 1:70); mp 189–191 °C (hexane/ CH_2Cl_2); IR (KBr) 1509 cm^{-1} ; ^1H NMR δ 2.07 (s, 3H), 2.31 (s, 3H), 6.86 (d, $J = 7.4$ Hz, 2H), 6.97–7.02 (m, 3H), 7.12 (dd, $J = 8.0, 7.4$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR δ 21.0, 36.8, 60.5, 126.8, 127.4, 127.9, 128.3, 129.0, 134.5, 135.1, 140.0, 145.6, 149.0. HR-MS (DART). Calcd for $\text{C}_{15}\text{H}_{15}\text{S}$: (M+H): 227.0894. Found: m/z 227.0887. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: C, 79.60; H, 6.23; S, 14.16. Found: C, 79.46; H, 6.27; S, 14.26.

8-(3-Chlorophenyl)-8-methyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4d). This product was purified by column chromatography. It was slightly less mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A white amorphous powder; R_f 0.39 ($\text{Et}_2\text{O}/\text{hexane}$ 1:50); IR (KBr) 1461 cm^{-1} ; ^1H NMR δ 2.05 (s, 3H), 6.87 (dt, $J = 6.9, 1.7$ Hz, 1H), 7.01 (dd, $J = 7.4, 1.1$ Hz, 1H), 6.97–7.00 (m, 1H), 7.13–7.17 (m, 3H), 7.28 (td, $J = 7.4, 1.1$ Hz, 2H); ^{13}C NMR δ 36.7, 60.3, 125.2, 126.0, 127.1, 127.8, 127.9, 128.9, 129.4, 133.6, 133.8, 140.5, 148.4, 150.7. HR-MS (FI). Calcd for $\text{C}_{14}\text{H}_{11}\text{ClS}$: (M): 246.0270. Found: m/z 246.0262.

8-(4-Chlorophenyl)-8-methyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4e). This product was purified by column chromatography. It was slightly less mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A white solid; R_f 0.38 ($\text{AcOEt}/\text{hexane}$ 1:20); mp 176–178 °C (hexane); IR (KBr) 1485 cm^{-1} ; ^1H NMR δ 2.04 (s, 3H), 6.88 (d, $J = 8.6$ Hz, 2H), 7.02 (td, $J = 7.4, 1.1$ Hz, 1H), 7.16 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 7.4$ Hz, 2H), 7.32 (dd, $J = 7.4, 1.1$ Hz, 1H); ^{13}C NMR δ 36.7, 60.2,

127.7, 127.8, 128.0, 128.2, 129.3, 131.4, 133.9, 140.2, 147.3, 148.4. HR-MS (DART). Calcd for $C_{14}H_{12}ClS$: (M+H): 247.0348. Found: m/z 247.0338. Anal. Calcd for $C_{14}H_{11}ClS$: C, 68.15; H, 4.49; S, 12.99. Found: C, 68.34; H, 4.84; S, 13.05.

8-(4-Methoxyphenyl)-8-methyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4f). This product was purified by column chromatography. It was slightly less mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A white solid; R_f 0.25 (AcOEt/hexane 1:12); mp 163–166 °C (hexane/AcOEt); IR (KBr) 1509 cm^{-1} ; 1H NMR δ 2.08 (s, 3H), 3.78 (s, 3H), 6.72 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 7.01 (td, $J = 7.4, 1.1$ Hz, 1H), 7.13 (ddd, $J = 8.0, 7.4, 1.7$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 7.35 (dd, $J = 7.4, 1.7$ Hz, 1H); ^{13}C NMR δ 36.7, 55.1, 60.1, 112.8, 127.4, 127.9, 128.0, 129.0, 134.5, 139.9, 140.8, 149.0, 157.4. HR-MS (DART). Calcd for $C_{15}H_{15}OS$: (M+H): 243.0843. Found: m/z 243.0839. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.35; H, 5.82; S, 13.23. Found: C, 74.13; H, 5.91; S, 13.34.

4-Chloro-8-methyl-8-phenyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4g). This product was purified by column chromatography. It is slightly more mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A pale-yellow solid; R_f 0.71 (Et₂O/hexane 1:80); mp 184–187 °C (hexane); IR (KBr) 1442 cm^{-1} ; 1H NMR δ 2.06 (s, 3H), 6.91 (dd, $J = 7.4, 1.7$ Hz, 2H), 7.17–7.20 (m, 3H), 7.26 (s, 2H), 7.36 (d, $J = 2.3$ Hz, 1H); ^{13}C NMR δ 36.6, 60.7, 126.0, 126.7, 127.7, 129.2, 129.3, 132.9, 136.1, 139.2, 147.4, 147.7. HR-MS (DART). Calcd for $C_{14}H_{12}ClS$: (M+H): 247.0348. Found: m/z 247.0342. Anal. Calcd for $C_{14}H_{11}ClS$: C, 68.15; H, 4.49. Found: C, 68.08; H, 4.53.

3-Chloro-8-methyl-8-phenyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4h). This product was purified by column chromatography. It was slightly more mobile and the benzoxathiinone intermediate was rather less mobile than the starting material. A white solid; R_f 0.50 (AcOEt/hexane 1:30); mp 199–203 °C (hexane); IR (KBr) 1492 cm^{-1} ; 1H NMR δ 2.05 (s, 3H), 6.93 (d, $J = 6.9$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 1H), 7.17–7.21 (m, 3H), 7.28 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR δ 36.6, 60.6, 126.0, 126.8, 127.71, 127.74, 128.5, 132.6, 135.7, 141.1, 147.5, 150.9. HR-MS (DART). Calcd for $C_{14}H_{12}ClS$: (M+H): 247.0348. Found: m/z 247.0343. Anal. Calcd for $C_{14}H_{11}ClS$: C, 68.15; H, 4.49. Found: C, 68.01; H, 4.51.

8-(4-Chlorophenyl)-3-methoxy-8-methyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4i). This product was purified by trituration with hexane. It was rather less mobile than the starting material and the benzoxathiinone intermediate was not observed during the reaction by analyses on TLC. A white solid; mp 224–226 °C (hexane/CH₂Cl₂); IR (KBr) 1489 cm^{-1} ; 1H NMR δ 1.99 (s, 3H), 3.73 (s, 3H), 6.55 (d, $J = 8.0$ Hz, 1H), 6.84 (s, 1H), 6.89 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR δ 36.6, 55.3, 59.8, 111.1, 116.1, 124.6, 127.6, 128.2, 131.4, 141.5, 147.1, 150.1, 160.3. HR-MS (DART). Calcd for $C_{15}H_{14}ClOS$: (M+H): 277.0454. Found: m/z 277.0448. Anal. Calcd for $C_{15}H_{13}ClOS$: C, 65.09; H, 4.73. Found: C, 64.95; H, 4.70.

3-Methoxy-8-(4-methoxyphenyl)-8-methyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4j). This product was

purified by trituration with hexane. It was rather less mobile than the starting material and the benzoxathiinone intermediate was not observed during the reaction by analyses on TLC. A white solid; mp 227–231 °C (hexane/CH₂Cl₂); IR (KBr) 1604, 1508 cm⁻¹; ¹H NMR δ 2.03 (s, 3H), 3.73 (s, 3H), 3.77 (s, 3H), 6.54 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.71 (d, *J* = 9.2 Hz, 2H), 6.85 (d, *J* = 2.9 Hz, 1H), 6.89 (d, *J* = 9.2 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 1H); ¹³C NMR δ 36.7, 55.1, 55.2, 59.7, 110.8, 112.8, 115.9, 125.3, 127.9, 140.6, 141.2, 150.7, 157.4, 160.1. HR-MS (DART). Calcd for C₁₆H₁₇O₂S (M+H): 273.0949. Found: *m/z* 273.0943. Anal. Calcd for C₁₆H₁₆O₂S: C, 70.56; H, 5.92. Found: C, 70.44; H, 6.20.

3,4-Dimethoxy-8-methyl-8-phenyl-7-thiabicyclo[4.2.0]octa-1,3,5-triene (4k). This product was purified by trituration with hexane. It was rather less mobile than the starting material and the benzoxathiinone intermediate, which was somewhat less mobile than the starting material, was observed during the reaction by analyses on TLC. A white solid; mp 169–171 °C (hexane/CH₂Cl₂); IR (KBr) 1504 cm⁻¹; ¹H NMR δ 2.08 (s, 3H), 3.800 (s, 3H), 3.804 (s, 3H), 6.83 (s, 1H), 6.88 (s, 1H), 6.97 (d, *J* = 7.4 Hz, 2H), 7.15–7.20 (m, 3H); ¹³C NMR δ 37.0, 55.9, 56.0, 60.4, 111.7, 122.6, 125.7, 125.8, 126.8, 127.5, 142.2, 147.2, 148.7, 149.1. HR-MS (ESI). Calcd for C₁₆H₁₇O₂S: (M+H): 273.0949. Found: *m/z* 273.0940. Anal. Calcd for C₁₆H₁₆O₂S: C, 70.56; H, 5.92. Found: C, 70.45; H, 5.82.

When the reactions using compounds (2a), (2e), and (2h) were carried out at 0 °C, the corresponding benzoxathiinones (3a), (3e), and (3h) could be isolated by column chromatography on SiO₂ (AcOEt/hexane 1:20).

4-Methyl-4-phenyl-4H-3,1-benzoxathiin-2-one (3a): a white solid; mp 97–99 °C (hexane); IR (neat) 1711 cm⁻¹; ¹H NMR δ 2.13 (s, 3H), 7.12–7.16 (m, 2H), 7.26–7.30 (m, 4H), 7.41–7.45 (m, 2H), 7.58 (dd, *J* = 8.6, 3.4 Hz, 1H); ¹³C NMR δ 28.9, 88.8, 125.4, 126.5, 126.8, 127.3, 128.3, 128.5, 129.4, 130.3, 134.5, 142.1, 166.0. HR-MS (ESI). Calcd for C₁₅H₁₂NaO₂S: (M+Na): 279.0456. Found: *m/z* 279.0450. Anal. Calcd for C₁₅H₁₂O₂S: C, 70.29; H, 4.72. Found: C, 70.35; H, 4.76.

4-(4-Chlorophenyl)-4-methyl-4H-3,1-benzoxathiin-2-one (3e): a white solid; mp 129–131 °C (hexane); IR (KBr) 1697 cm⁻¹; ¹H NMR δ 2.11 (s, 3H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.25–7.30 (m, 3H), 7.42–7.46 (m, 2H), 7.54–7.57 (m, 1H); ¹³C NMR δ 28.8, 88.3, 126.4, 126.9, 127.0, 127.5, 128.7, 129.6, 130.1, 134.0, 134.3, 140.7, 165.7. HR-MS (DART). Calcd for C₁₅H₁₂ClO₂S: (M+H): 291.0246. Found: *m/z* 291.0236. Anal. Calcd for C₁₅H₁₁ClO₂S: C, 61.96; H, 3.81; S, 11.03. Found: C, 61.72; H, 3.83; S, 11.37.

6-Chloro-4-methyl-4-phenyl-4H-3,1-benzoxathiin-2-one (3h): a white solid; mp 101–103 °C (hexane); IR (KBr) 1698 cm⁻¹; ¹H NMR δ 2.11 (s, 3H), 7.12–7.16 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.29–7.32 (m, 3H), 7.41 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.55 (d, *J* = 2.3 Hz, 1H); ¹³C NMR δ 28.8, 88.5, 125.4, 126.9, 128.0, 128.6, 128.7, 128.9, 129.5, 133.5, 136.4, 141.4, 165.1. HR-MS (DART). Calcd for C₁₅H₁₂ClO₂S: (M+H): 291.0246. Found: *m/z* 291.0241. Anal. Calcd for C₁₅H₁₁ClO₂S: C, 61.96; H, 3.81. Found: C, 62.00; H,

3.76.

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